

Title: MINERAL GEAR OILS AND TRANSMISSION FLUIDS**Cross Reference to Related Application**

This application claims priority from provisional application Serial No. 60/135,484, filed May 24, 1999, the entire disclosure which is hereby incorporated by reference.

Technical Field of the Invention

This invention relates to lubricants formed with specific mineral base oils. More specifically, the invention relates to gear oils and transmission fluids which contain a mineral oil of lubricating viscosity which has an iodine number of less than 9 and has a higher percentage of paraffinic saturates than cycloparaffinic saturates.

Background of the Invention

Gear oils and transmission fluids have been required recently to provide effective lubrication even in systems which are exposed to longer drain intervals and to higher temperatures. When the lubricant is exposed to these high temperatures, oxidation of the base oil occurs, usually at the points of unsaturation of the oils used in the lubricant. This oxidation leads to unacceptable viscosity change (increase) and reduced effectiveness of the lubricants.

Lubricant formulators have sought to provide lubricants which have improved oxidation stability. Polyalphaolefins have been used as an alternative to mineral oils. The polyalphaolefins have low levels unsaturation and have good high temperature performance properties. However, polyalphaolefins are more expensive than mineral oils. Also, the polyalphaolefins generally have better low temperature performance than mineral oils.

Mineral oils have been developed which provide improved oxidation properties. These mineral oils are generally referred to as Group II and Group III basestocks. These basestocks were developed for passenger car lubricants. These basestocks cost less than polyalphaolefins. The Group II basestocks are generally worse in oxidation and low temperature performance than Group III basestocks. Group II and III basestocks have a high level of saturation. However, Applicants have discovered that oxidation and low temperature performance are affected by the type of saturated components in the oil. Group II stocks generally have a higher proportion of cyclic saturated components than aliphatic saturated components.

The type of environment affects the oxidation of basestocks. In the passenger car motor oil area, the form of oxidation is caused by the increased acidic blow by-products from combustion of fuel in the engines, either diesel or gasoline fuel. These acidic combustion products act together with oxygen to enhance oxidation of the oils. In the gear and transmission area, the oxidation is different than those in passenger car motor oils. There are no acidic blow by-products to enhance oxidation of the oils.

It is desirable to have a Group III based transmission or gear lubricant which provides good oxidation performance.

Summary of the Invention

This invention relates to mineral oil based gear oils and transmission fluids which comprise a major amount of a mineral oil having an iodine number of less than 9 and where at least 55% of the saturates are aliphatic, and gear oil or transmission fluid additives. In one embodiment, the invention relates to a gear oil or transmission fluid composition comprising a major amount of lubricant basestock and at least one functional additive wherein a major amount of the lubricant

basestock comprises a mineral oil having an iodine number of less than 9 and comprising at least 45% by weight of aliphatic saturates. These gear oils and transmission fluids have good viscosity and oxidation properties.

Detailed Description of the Preferred Embodiments

The term "hydrocarbyl" includes hydrocarbon as well as substantially hydrocarbon groups. Substantially hydrocarbon describes groups which contain heteroatom substituents that do not alter the predominantly hydrocarbon nature of the substituent. Examples of hydrocarbyl groups include the following:

(1) hydrocarbon substituents, i.e., aliphatic (e.g., alkyl or alkenyl) and alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic substituents and the like as well as cyclic substituents wherein the ring is completed through another portion of the molecule (that is, for example, any two indicated substituents may together form an alicyclic radical);

(2) substituted hydrocarbon substituents, i.e., those substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; those skilled in the art will be aware of such groups (e.g., halo (especially chloro and fluoro), hydroxy, mercapto, nitro, nitroso, sulfoxy, etc.);

(3) heteroatom substituents, i.e., substituents which will, while having a predominantly hydrocarbon character within the context of this invention, contain an atom other than carbon present in a ring or chain otherwise composed of carbon atoms (e.g., alkoxy or alkylthio). Suitable heteroatoms will be apparent to those of ordinary skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as, e.g. parietal, furyl, thienyl, imidazolyl, etc.

In general, no more than about 2, preferably no more than one heteroatom substituent will be present for every ten carbon atoms in the hydrocarbyl group. Typically, there will be no such heteroatom substituents in the hydrocarbyl group. Therefore, the hydrocarbyl group is purely hydrocarbon.

As previously indicated, the above combination of components are useful in lubricants where they can be used in automatic or manual transmission fluids, transaxle lubricants, gear lubricants, both for open and enclosed systems, tractor lubricants, metal-working lubricants, hydraulic fluids and other lubricating oil and grease compositions. In one embodiment, the lubricants contain less than 3% by weight water, or less than 2% by weight water, or less than 1% by weight water.

The lubricants of the present invention include automatic transmission, manual transmission and gear lubricants. The transmission lubricants include those that meet the General Motor Dextron® III and Ford Mercon® automatic transmission fluid requirements. In one embodiment, the lubricants include heavy duty or off road transmissions such as those that meet the Allison C-4 specification. In another embodiment, the lubricants are gear lubricants and include GL4, or GL5 lubricants. Additionally, in another embodiment, the lubricants are MT-1 lubricants.

As described herein, the present invention relates to gear oil transmission fluid compositions which comprises a major amount of a basestock. The basestock is combined with functional additives to form the gear oil and transmission fluids. The basestock may be a singular component or may be a combination of components to be combined with functional additives to form the gear oil or transmission fluid. In one embodiment, the basestock comprises a major amount of the mineral oils discussed below (e.g., those having a high level of aliphatic saturates and a low iodine number). The minority of the basestock may be composed of other mineral oils or polyalphaolefins. Generally speaking, the basestocks are composed of at least about 60%, or at least about 75%, or at least about 85% by weight of the mineral oils discussed below (Group III basestocks). The gear oils and transmission fluid compositions of the present invention may additionally contain at least one functional additive. The functional additive adds an additional characteristic to the compositions in addition those properties provided by the basestock and/or polymer or fluidizing agent. Examples of such functions includes antiwear, extreme pressure, antioxidation, fluidity, friction modification, etc.

Mineral oils

As discussed above, the mineral oils have an iodine number of less than 9 and have at least about 45% of the saturates present as aliphatic saturates. Iodine value is determined according to ASTM D-460. In one embodiment, the mineral oil has a iodine value less than about 8, or less than about 6, or less than about 4. The saturates level are determined by mass spectrometer. By mass spectroscopy, Group I stocks have about 70% saturates, Group II stocks have about 95% to about 98% saturates and Group III stocks have about 98%-100% saturates. Group II stocks have greater than 50% of their saturates present as cycloparaffinic compounds. The saturates of the mineral oils used in the present invention typically have at least about 45%, or at least about 50%, or at least about 60% aliphatic saturates. These aliphatic saturates are often referred to as paraffinic saturates. The cyclic saturates are generally referred to as cycloparaffinic saturates. Cyclic saturates compose the balance of the saturates in the mineral oils. The inventors have discovered that mineral oils having a higher proportion of aliphatic saturates have better oxidation properties and low temperature properties.

In one embodiment, the lubricating compositions are prepared from a mineral oil having a kinematic viscosity of less than 8, or less than about 7, or less than about 6 cSt at 100°C. Of course, it is understood that the mineral oil must have sufficient viscosity to act as a lubricating oil. Typically, the mineral oil has a kinematic viscosity of at least about 2, or at least about 3, or at least about 4 cSt at 100°C. In one embodiment, the kinematic viscosity of the mineral oils is from about 3.0 to about 7.5, or from about 3.3 to about 7.0, or from about 3.4 to about 6.5. Typically, the mineral oils will have an SAE designation up to about 250 N, or up to about 150 N. Useful oils include 70N, 100N, 130N, 150N and 200N mineral oils.

As use herein the term "mineral oil" refers to oils of lubricating viscosity which are derived from petroleum crude. The petroleum crudes may be subjected to processing such as hydroprocessing, hydrocracking, and isomerizing. Hydroprocessing includes processes such as sequential isocracking, isodewaxing

and hydrofinishing. These mineral oils are those referred to as Group III basestock or base oils. In one embodiment, the mineral oil has less than 0.3% or less than 0.1% sulfur. In another embodiment, the oils of lubricating viscosity generally have a viscosity index of 120 or more.

5 Examples of useful oils of lubricating viscosity include HVI and XHVI basestocks, such isomerized wax base oils and UCBO (Unconventional Base Oils) base oils. Specific examples of these base oils include 100N isomerized wax basestock (0.01% sulfur/ 141 VI), 120N isomerized wax basestock (0.01% sulfur/ 149 VI), 170N isomerized wax basestock (0.01% sulfur/ 142 VI), and 250N isomerized wax basestock (0.01% sulfur/ 146 VI); refined basestocks, such as 250N solvent refined paraffinic mineral oil (0.16% sulfur/89 VI), 200N solvent refined naphthenic mineral oil (0.2% sulfur/ 60 VI), 100N solvent refined/ hydrotreated paraffinic mineral oil (0.01% sulfur/98 VI), 240N solvent refined/ hydrotreated paraffinic mineral oil (0.01% sulfur/ 98 VI), 80N solvent refined/ hydrotreated paraffinic mineral oil (0.08% sulfur/ 127 VI), and 150N solvent refined/ hydrotreated paraffinic mineral oil (0.17% sulfur/ 127 VI). Further examples of the mineral oils include those Group III basestocks made by Texaco such as the TEXHVI stocks which include TEXHVI-100N (95% saturates, 125 viscosity index and 0.02% sulfur); TEXHVI-70N (97.8% saturates, 123 viscosity index and 0.02% sulfur); Texaco "MOTIVA" TEXHVI 90N-100N (100% saturates, 125 viscosity index and 0.01% sulfur); and "MOTIVA" TEXHVI 75N (100% saturates, 125 viscosity index and 0.0% sulfur). Examples of useful Group III basestocks made by Chevron include UCBO 200N (100% saturates, 142 viscosity index and 0.005% sulfur); UCBO 100N (100% saturates, 129 viscosity index, and 0.004% sulfur).

Polymers

The lubricating compositions may additionally contain (A) at least one polymer. The polymer generally is present in an amount from about 3% to about 40%, or from about 5% to about 35%, or from about 10% to about 30% by weight

of the lubricating composition. The polymers include a polyalkene or derivative thereof, an ethylene- α -olefin copolymer, an ethylene-propylene polymer, an α -olefin-unsaturated carboxylic reagent copolymer, a polyacrylate, a polymethacrylate, a hydrogenated interpolymer of an alkenylarene and a conjugated diene, and mixtures thereof. Here, and elsewhere in the specification and claims, any member of a genus (or list) may be excluded from claims.

In one embodiment, the polymer (A) is characterized by an \bar{M}_w (weight average molecular weight) of less than about 50,000, or less than about 45,000, or less than about 40,000. In one embodiment, the polymer has an \bar{M}_w of less than about 25,000, or less than about 10,000, or less than about 7,000. Typically the polymer has an \bar{M}_w of at least about 1,000, or at least about 2,000, or at least about 3,000. In one embodiment, the polymer (A) is characterized by an \bar{M}_n (number average molecular weight) of up to about 6000, or up to about 5000. Generally, the polymer is characterized by having an \bar{M}_n from about 800 to about 6000, or from about 900 to about 5000, or from about 1000 to 4000. In another embodiment, the polymers have a \bar{M}_n from about 1300 to about 5000, or from about 1500 to about 4500, or from about 1700 to about 3000. The polymers also generally have a \bar{M}_w/\bar{M}_n from about 1.5 to about 8, or from about 1.8 to about 6.5, or from about 2 to about 5.5.

In one embodiment, the polymer may be a sheared polymer of higher molecular weight, e.g. greater than \bar{M}_w 50,000. In this embodiment, a higher molecular weight polymer is sheared to the desired molecular weight. The shearing may be done in any suitable apparatus, such as an extruder, an injector, an FZG apparatus, etc.

The abbreviation \bar{M}_w and \bar{M}_n is the conventional symbol representing weight average and number average molecular weight, respectively. Gel permeation chromatography (GPC) is a method which provides both molecular weights as well as the entire molecular weight distribution of the polymers. For purpose of this invention a series of fractionated polymers of isobutene, polyisobutene, is used as

the calibration standard in the GPC. The techniques for determining \bar{M}_n and \bar{M}_w values of polymers are well known and are described in numerous books and articles. For example, methods for the determination of \bar{M}_n and molecular weight distribution of polymers is described in W.W. Yan, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatographs", J. Wiley & Sons, Inc., 1979.

In one embodiment, the polymer (A) is a polyalkene. The polyalkene includes homopolymers and interpolymers of olefins having from 2 to about 40, or from 3 to about 24, or from 4 to about 12 carbon atoms. The olefins may be monoolefins, such as ethylene, propylene, 1-butene, isobutene, an α -olefin, or polyolefinic monomers, including diolefinic monomers, such 1,3-butadiene and isoprene. The α -olefins generally have from about 4 to about 30, or from about 8 to about 18 carbon atoms. These olefins are sometimes referred to as mono-1-olefins or terminal olefins. The α -olefins and isomerized α -olefins include 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tetracosene, etc. Commercially available α -olefin fractions that can be used include the C_{15-18} α -olefins, C_{12-16} α -olefins, C_{14-16} α -olefins, C_{14-18} α -olefins, C_{16-18} α -olefins, C_{16-20} α -olefins, C_{18-24} α -olefins, C_{22-28} α -olefins, etc. The polyalkenes are prepared by conventional procedures. The polyalkenes are described in U.S. Patent 3,219,666 and 4,234,435, the disclosures of which is hereby incorporated by reference. Examples of polyalkenes includes polypropylenes, polybutylenes, polyisoprene and polybutadienes. In one embodiment, the polyalkene is a homopolymer, such as a polybutene. One example of a useful polybutene is a polymer where about 50% of the polymer is derived from isobutylene. Useful polybutenes include those having an \bar{M}_w of about 4,000 to about 8,000, preferably 6,700.

In one embodiment, the polyalkene is derived from one or more dienes. The dienes include 1,3 pentadiene, isoprene, methylisoprene, 1,4-hexadiene, 1,5-hepatadiene, 1-6-octadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene,

linear 1,3-conjugated dienes (e.g. 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and 1,3-hexadiene) and cyclic dienes (e.g. cyclopentadiene, dicyclopentadiene, fulvene, 1,3-cyclohexadiene, 1,3,5-cycloheptatriene, and cyclooctatetraene). The polyalkene may be a homopolymer of a diene, or a co- or terpolymer of a diene with either another diene or one or more of the above monoolefins. The polyalkene may be hydrogenated. A commercially available polyalkene derived from at least one diene is LIR-290, a hydrogenated polyisoprene ($\bar{M}_w=25,000$), available commercially from Kuraray Co, Ltd.

In another embodiment, the polymer is a derivative of a polyalkene. The derivatives are typically prepared by reacting one or more of the above polyalkenes or a halogenated derivative thereof with an unsaturated reagent. The halogenated polyalkenes are prepared by reacting a polyalkene with a halogen gas, such as chlorine. The preparation of these materials is known to those in the art. The unsaturated reagents include unsaturated amines, ethers, and unsaturated carboxylic reagents, such as unsaturated acids, esters, and anhydrides. Examples of unsaturated amines include unsaturated amides, unsaturated imides, and nitrogen containing acrylate and methacrylate esters. Specific examples of unsaturated amines include acrylamide, N,N'-methylene bis(acrylamide), methacrylamide, crotonamide, N-(3,6-diazaheptyl) maleimide, N-(3-dimethylaminopropyl) maleimide, N-(2-methoxyethoxyethyl) maleimide, N-vinyl pyrrolidinone, 2- or 4-vinyl pyridine, dimethylaminoethyl methacrylate and the like.

In one embodiment, the unsaturated carboxylic reagent is an acid, anhydride, ester, or mixtures thereof. If an ester is desired, it can be prepared by reacting an unsaturated carboxylic acid or anhydride with a polyalkene or halogenated derivative thereof and subsequently reacting the reaction product with an alcohol to form the ester. The unsaturated carboxylic reagents include acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, 2-phenylpropenoic acid, maleic acid, maleic anhydride, fumaric acid, mesaconic acid, itaconic acid and citraconic acid maleic, fumaric, acrylic, methacrylic, itaconic, and citraconic acids, esters, and

anhydrides (where possible). The esters may be represented by one of the formulae: $(R_1)_2C=C(R_1)C(O)OR_2$, or $R_2O-(O)C-HC=CH-C(O)OR_2$, wherein each R_1 and R_2 are independently hydrogen or a hydrocarbyl group having 1 to about 30, or to about 12, or to about 8 carbon atoms, R_1 is hydrogen or an alkyl group having from 1 to about 6 carbon atoms. In one embodiment, R_1 is preferably hydrogen or a methyl group. In another embodiment, R_2 is an alkyl or hydroxyalkyl group having from about 1 to about 30, or from 2 to about 24, or from about 3 to about 18 carbon atoms. R_2 may be derived from one or more alcohols described below. Unsaturated carboxylic esters include methyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, ethyl maleate, butyl maleate and 2-ethylhexyl maleate. The above list includes mono- as well as diesters of maleic, fumaric, and itaconic acids and anhydrides.

The polyalkene derivatives are prepared by means known to those in the art. These materials have been referred to as hydrocarbyl substituted carboxylic acylating agents, and are discussed below. U. S. Patents 3,219,666 and 4,234,435 describe the polyalkene derivatives and methods of making the same and are incorporated for such descriptions.

In another embodiment, the polymer (A) is an ethylene- α -olefin copolymer. Typically, the copolymer is a random copolymer. The copolymer generally has from about 30% to about 80%, or from about 50% to about 75% by mole of ethylene. The α -olefins include butene, pentene, hexene or one more of the described above described α -olefins. In one embodiment, the α -olefin contains from about 3 to about 20, or from about 4 to about 12 carbon atoms. In one embodiment, the ethylene- α -olefin copolymers have an \bar{M}_w from about 10,000 up to about 40,000, or from about 15,000 up to about 35,000, or from about 20,000 up to about 30,000. In another embodiment, the ethylene- α -olefin copolymers have an \bar{M}_n from about 800 to about 6000, or from about 1500 to about 5000, or from about 2000 to about 4500. Examples of ethylene α -olefins copolymers include ethylene-butene copolymers and

ethylene-octene copolymers. Examples of commercially available copolymers include Lucant HC 600 and Lucant HC 2000 ($\bar{M}_w=25,000$), available from Mitsui Petrochemical Co., Ltd.

In another embodiment, the polymer (A) is an ethylene propylene polymer. These polymers include ethylene propylene copolymers and ethylene propylene terpolymers. When the ethylene propylene polymer is an ethylene propylene copolymer (EPM, also called EPR polymers), it may be formed by copolymerization of ethylene and propylene under known conditions, preferably Ziegler-Natta reaction conditions. The preferred ethylene propylene copolymers contain units derived from ethylene in an amount from about 40% to about 70%, or from about 50% to about 60%, or about 55% by mole, the remainder being derived from propylene. The molecular weight distribution may be characterized by a polydispersity (\bar{M}_w/\bar{M}_n) from about 1 to about 8, or from about 1.2 to about 4.

In another embodiment, the ethylene propylene polymer is a terpolymer of ethylene, propylene and a diene monomer. In one embodiment, the diene is a conjugated diene. The dienes are disclosed above. The terpolymers are produced under similar conditions as those of the ethylene propylene copolymers. The preferred terpolymers contain units derived from ethylene in amount from about 10% to about 80%, or from about 25% to about 85%, or about 35% to about 60% by mole, and units derived from propylene in amount from about 15% to about 70%, or from about 30% to about 60% by mole, and units derived from diene third monomer in amount from about 0.5% to about 20%, or from about 1% to about 10%, or about 2% to about 8% by mole. The following table contains examples of ethylene propylene terpolymers.

Example	Ethylene	Propylene	Diene
A	42%*	53%	5% 1,5 heptadiene
B	48%	48%	4% dicyclopentadiene
C	45%	48%	10% 5-ethylidene-2-norbornene
D	45%	48%	4% 1,6 octadiene
E	48%	48%	4%, 4 cyclohexadiene
F	50%	45%	4% 5-methylene-2-norbornene

*Percentages are by mole

In one embodiment, the ethylene propylene polymer is a terpolymer of ethylene, propylene and dicyclopentadiene or ethylidene norbornene, available commercially as Trilene elastomers from the Uniroyal Corporation. A useful ethylene propylene terpolymer is Trilene CP-40. The ethylene propylene polymers are prepared by means known to those in the art. U.S. Patent No. 3,691,078 describes ethylene propylene polymers and methods of preparing them, and is incorporated by reference for such disclosures.

In another embodiment, the polymer (A) is a copolymer of an α -olefin and an unsaturated reagent. The α -olefins may be any of those discussed above, and include propylene, 1-butene, 2-methyl propene, 2-methyl-1-octene, and 1-decene. The unsaturated reagents are described above. The unsaturated carboxylic reagents include acrylates, methacrylates, maleates and fumarates. The α -olefin-unsaturated carboxylic reagent polymers are prepared by means known to those in the art. Examples of α -olefin-unsaturated carboxylic reagent copolymers include poly(octene-co-ethylacrylate), poly(decene-co-butylmethacrylate), poly(hexene-co-maleic anhydride), poly(octene-co-methyl fumarate) and the like.

In another embodiment, the polymer (A) is a polyacrylate or polymethacrylate. The polyacrylates and polymethacrylates include homopolymers

and interpolymers of one or more of the above described acrylic or methacrylic acids or esters. The polyacrylates and polymethacrylates include the Acryloid 1019 polymers, available from Rohm and Haas Company, Garbacryl 6335 available from Societe Francaise d'Organo-Sythese (SFOS), LZ 7720C available from The Lubrizol Corporation, and Viscoplex 0-101 polymers, available from Rohm Darmstadt.

In another embodiment, the polymer (A) is a hydrogenated interpolymers of an vinyl substituted aromatic compound and a conjugated diene. The interpolymers include diblock, triblock and random block interpolymers. The vinyl substituted aromatic compounds generally have from about 8 to about 20, or from about 8 to about 18, or from about 8 to about 12 carbon atoms. Examples of vinyl substituted aromatics include styrene, α -methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-t-butylstyrene, with styrene being preferred. The conjugated dienes are described above. Isoprene and 1,3-butadiene are preferred conjugated dienes.

The vinyl substituted aromatic content of these copolymers is in the range from about 20% to about 70%, or from about 40% to about 60% by weight. Thus, the conjugated diene content is in the range from about 30% to about 80%, or from about 40% to about 60% by weight. These interpolymers are prepared by conventional methods well known in the art. Such copolymers usually are prepared by anionic polymerization using, for example, an alkali metal hydrocarbon (e.g., sec-butyllithium) as a polymerization catalyst. Examples of suitable hydrogenated copolymers of a vinyl substituted aromatic compound and a conjugated diene include Shellvis-40, and Shellvis-50, both hydrogenated styrene-isoprene block copolymers, manufactured by Shell Chemicals.

Fluidizing Agents (B)

The lubricating compositions may additionally contain (B) at least one fluidizing agent. Generally, the fluidizing agent (B) is present in an amount up to about 30% by weight. Typically the fluidizing agent is present in an amount from

about 3% to about 30%, or from about 5% to about 28%, from about 10% to about 27%, or from about 15% to about 25% by weight of the lubricating composition. The amount of fluidizing agent equals the total amount of fluidizing agents in the lubricating compositions.

5 In one embodiment, the fluidizing agent (B) is at least one member selected from the group consisting of an alkylated aromatic hydrocarbon, a naphthenic oil, a poly α -olefin having a kinematic viscosity from about 3 to about 20 cSt at 100°C, a carboxylic acid esters, and mixtures of two or more thereof. The alkylated aromatic hydrocarbons typically include mono- or di- (more preferably mono-) substituted benzenes wherein the substituents are hydrocarbon-based groups
10 having from about 8 to about 30, or from about 10 to about 14 carbon atoms. An example is Alkylate A- 215 (a 237 molecular weight alkylated benzene) and Alkylate A-230 (a 230 molecular weight alkylated benzene) available from Monsanto.

The naphthenic oils are those derived from naphthenic crudes such as found
15 in the Louisiana area. The viscosity of such naphthenic oils at 40°C generally is less than 4 centistokes and more generally within the range of from about 3.0 to about 3.8 centistokes. At 100°C the viscosity of the desirable naphthenic crudes is within the range of about 0.8 to about 1.6 centistokes.

The poly α -olefins (PAOs) are derived from monomers having from about 4
20 to about 30, or from about 4 to about 20, or from about 6 to about 16 carbon atoms. Examples of useful PAOs include those derived from one or more of the above olefins, such as the α -olefins. These PAOs may have a viscosity from about 2 to about 30, or from about 3 to about 20, or from about 3 to about 8 cSt at 100°C. Examples of PAOs include 4 cSt poly α -olefins, 6 cSt poly α -olefins, and 8 cSt poly α -olefins. A particularly useful PAO is derived from decene. When the poly α -olefin
25 is the fluidizing agent, then the poly α -olefin is present in an amount up to about 12% by weight.

The carboxylic ester fluidizing agents are reaction products of dicarboxylic esters with alcohols having from about 1 to about 30, or from about 2 to about 18,

or from about 3 to about 12 carbon atoms. The alcohols are described below and include methyl, ethyl, propyl, butyl, hexyl, heptyl, octyl, decyl and dodecyl alcohols. The dicarboxylic acids generally contain from about 4 to about 18, or from about 4 to about 12, or from about 4 to about 8 carbon atoms. Examples of dicarboxylic acids include phthalic acid, succinic acid, alkyl (C_{1-24})succinic acids, azelaic acid, adipic acid, and malonic acid. Particularly useful esters are dicarboxylic esters of C_{1-12} alcohols, such as esters of propyl, butyl, pentyl, hexyl, and octyl alcohols and azelaic acid. In one embodiment, the lubricating compositions contain less than about 20%, or less than about 15% by weight of carboxylic ester fluidizing agent.

Antiwear or Extreme Pressure Agent (C)

In one embodiment, the lubricating compositions and concentrates include (C) at least one antiwear or extreme pressure agent. The antiwear or extreme pressure agent generally is each present in amounts from about 0.05% to about 10%, or from about 0.1% to about 8%, or from about 0.3% to about 7%, or from about 0.5% to about 5% by weight. In another embodiment, (C) is present in an amount from about 0.5% to about 10%, preferably from about 1% to about 7%, or from about 2% to about 6% by weight. In one embodiment, (C) is at least one member selected from a sulfur compound, a phosphorus containing compound, a boron containing compound, and mixtures of two or more thereof.

Sulfur Compounds

The sulfur containing antiwear and/or extreme pressure agents include sulfurized compounds, such as sulfurized olefins, metal and ashless dithiocarbamates, or mixtures of two or more thereof. The sulfur compounds include mono- or polysulfide compositions, and mixtures of mono and polysulfide. The sulfur compounds are generally characterized as having sulfide linkages containing an average from 1 to about 10, or from about 2 to about 8, or from about 3 to about 4 sulfur atoms. In one embodiment, the sulfur compound may be a

mixture of di-, tri- or tetrasulfide materials, preferably having a majority of trisulfide. In one embodiment, the materials have at least 70% trisulfide greater than 80% trisulfide.

5 The sulfur containing antiwear and/or extreme pressure agent includes sulfurized compounds, such as sulfurized olefins, metal containing and ashless dithiocarbamates, or mixtures of two or more thereof. The sulfur compounds include mono- or polysulfide compositions, and mixtures of mono and polysulfide compositions.

10 Materials which may be sulfurized to form the sulfur compounds include oils, unsaturated fatty acids, unsaturated fatty esters, olefins, terpenes, or Diels-Alder adducts. Oils which may be sulfurized are mineral or synthetic oils, including mineral oils, lard oil, carboxylic acid esters derived from aliphatic alcohols and fatty acids or aliphatic carboxylic acids (e.g., myristyl oleate and oleyl oleate), and synthetic sperm whale oil substitutes and synthetic unsaturated esters or glycerides. 15 U. S. Patents 3,926,822 and 3,955,347, both issued to Habiby teach oils and sulfurized products may therefrom. These patents are incorporated by reference.

20 The unsaturated fatty acids generally contain from about 8 to about 30, or from about 12 to about 24 carbon atoms. Examples of unsaturated fatty acids include palmitoleic acid, oleic acid, linoleic acid, linolenic acid, erucic acid, lard oil acid, soybean oil acid, tall oil acid and rosin acid. The unsaturated fatty esters include fatty oils, that is, naturally occurring or synthetic esters of glycerol and one or more of the above unsaturated fatty acids. Examples of fatty esters include animal fats, such as Neat's-foot oil, lard oil, depot fat, beef tallow, vegetable oils such as cottonseed oil, corn oil, safflower oil, sesame oil, soybean oil, and sunflower 25 seed oil. The unsaturated fatty esters also may be prepared by esterifying a fatty acid with alcohols and polyols. The alcohols include mono- and polyhydric alcohols, such as methanol, ethanol, propanol, butanol, ethylene glycol, neopentyl glycol, glycerol and others described below.

The olefins, which may be sulfurized, contain at least one olefinic double bond, which is defined as a non-aromatic double bond. The olefins include the olefins and the dienes described above for preparing the polyalkenes. In its
5 broadest sense, the olefin may be defined by the formula $R^1R^2C=CR^3R^4$, wherein each of R^1 , R^2 , R^3 , and R^4 is hydrogen, or an organic group. In general, the R groups in the above formula which are not hydrogen may be represented by $-(CH_2)_n-A$, wherein n is a number from 0 to about 10 and A is represented by $-C(R^5)_3$, $-COOR^5$, $-CON(R^5)_2$, $-COON(R^5)_4$, $-COOM$, $-CN$, $-X$, $-YR^5$ or $-Ar$, wherein:
10 each R^5 is independently hydrogen, or a hydrocarbonyl group, with the proviso that any two R^5 groups may be connected to form a ring of up to about 12 carbon atoms; M is one equivalent of a metal cation (preferably Group I or II, e.g., sodium, potassium, barium, or calcium); X is halogen (e.g., chloro, bromo, or iodo); Y is oxygen or divalent sulfur; Ar is an aromatic group of up to about 12 carbon atoms.

The olefinic compound is usually one in which each R group which is not
15 hydrogen is independently alkyl, alkenyl or aryl group. In one embodiment, R^3 and R^4 are hydrogen and R^1 and R^2 are alkyl or aryl, especially alkyl having from 1 to about 30, or to about 16, or to about 8, or to about 4 carbon atoms. Olefins having from 2 to about 30, or from about 3 to about 16 (most often less than about 9) carbon atoms are particularly useful. Olefins having from 2 to about 5, or from 2
20 to about 4 carbon atoms are particularly useful. Isobutene, propylene and their dimers, trimers and tetramers, and mixtures thereof are especially preferred olefins. Of these compounds, isobutylene and diisobutylene are particularly desirable. The sulfur compound may be prepared by the sulfochlorination of olefins containing four or more carbon atoms and further treatment with inorganic higher polysulfides according to U.S. Patent 2,708,199. In another embodiment, the sulfur compounds
25 may be produced by sulfochlorination olefins, and further treatment with an alkali metal sulfide in the presence of free sulfur, and finally reacting that product with an

inorganic base. This procedure is described in U.S. Patent 3,471,404, and this disclosure is hereby incorporated by reference for its discussion of this procedure for preparing sulfurized olefins and the sulfurized olefins thus produced.

5 In one embodiment, the sulfur compound is an organic polysulfide. The sulfur compound may also be prepared by reacting, under superatmospheric pressure, the olefin with a mixture of sulfur and hydrogen sulfide in the presence, or absence, of a catalyst, followed by removal of low boiling materials. The olefins which may be sulfurized, the sulfurized olefin, and methods of preparing the same are described in U.S. Patents 4,119,549, 4,199,550, 4,191,659, and 4,344,854.
10 The disclosure of these patents is hereby incorporated by reference for its description of the sulfurized olefins and preparation of the same.

In one embodiment, the organic polysulfide is a mixture comprising at least about 90% dihydrocarbyl trisulfide, from about 0.1%, or from about 0.5% to about 8% dihydrocarbyl disulfide, and less than about 5% dihydrocarbyl higher polysulfides. Higher polysulfides are defined as containing four or more sulfide linkages. In one embodiment, the amount of trisulfide is at least about 92%, or preferably at least about 93%. In another embodiment, the amount of dihydrocarbyl higher polysulfides is less than 4%, or preferably less than about 3%. In one embodiment, the dihydrocarbyl disulfide is present in an amount from about 0.1%,
15 or from about 0.5% to about 5%, or from about 0.6% to about 3%.
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The sulfide analysis is performed on a Varian 6000 Gas Chromatograph and FID detector SP-4100 computing integrator. The Column is a 25 m. Megabore SGE BP-1. The temperature profile is 75°C, hold 2 min., to 250°C at 6°C/min. The helium flow is 6.0 ml/min plus make-up. The injection temperature is 200°C and the
25 detector temperature is 260°C. The injection size is 0.6 ul. References are the monosulfide, disulfide and trisulfide analogues to the sulfur composition for analysis. The references may be obtained by fractionating the product to form sulfide fractions (S1, S2 and S3) to be used for analysis. The procedure for analysis is as follows. (1) An area % determination is run on each of the reference samples to

determine its purity. (2) An area % determination is run on the sample to be tested to get a general idea of its composition. (3) A calibration blend is accurately weighed based on the area % results of the sample to be tested: then the internal standard toluene, is added to the blend in an amount equal to approximately one-half of the weight of the largest component. (This should give an area approximately the same as that of the largest component.) (4) The weights of each component (i.e., S-1, S-2 and S-3) are corrected by the % purity from step 1. (5) The calibration blend is run in triplicate using the corrected weights and then calculated, using the following formula, to reflect the multiple peaks in S-1 and S-2:

$$RF = \frac{(\text{concentration of components}^*) (\text{area of internal standard})}{(\text{total area of peaks}) (\text{concentration of internal standard})}$$

*Adjusted for purity of the standard i.e.: component weight times percent purity equals concentration of component.

(6) These response factors, plus the response factor for the single S-3 peak are used for determining weight percent results for the samples to be tested. (7) Results for S-1 and S-2 are adjusted to include all the peaks attributed to them. (8) Higher polysulfides are determined by difference using the following formula:

$S-4 = 100\% - (S-1 + S-2 + S-3 + \text{light ends})$ Light ends are defined as any peaks eluded prior to the internal standard.

In one embodiment, the sulfur compound is prepared by reacting, optionally under superatmospheric pressure, one or more of the above olefins with a mixture of sulfur and hydrogen sulfide in the presence, or absence, of a catalyst, such as an alkylamine catalyst, followed by removal of low boiling materials. The olefins which may be sulfurized, the sulfurized olefin, and methods of preparing the same are described in U.S. Patents 4,119,549, 4,199,550, 4,191,659, and 4,344,854. The disclosure of these patents is hereby incorporated by reference for its description of the sulfurized olefins and preparation of the same. The polysulfide

thus produced is fractionally distilled. In one aspect, the fractional distillation occurs under subatmospheric pressure. Typically the distillation pressure is from about 1 to about 250, from about 1 to about 100, or from about 1 to about 25 mm Hg. A fractionation column such as Snyder fractionation column may be used. In one embodiment, the fractionation is carried out at a reflux ratio from about 1:1 to about 15:1, or from about 2:1 to about 10:1, or from about 3:1 to about 8:1. The fraction distillation occurs at a temperature at which the sulfur composition which is being fractionated boils. Typically the fractional distillation occurs at a pot temperature from about 75°C to about 300°C, or from about 90°C to about 200°C.

The conditions of fractional distillation are determined by the sulfur composition being distilled. Typically, the sulfur compound is heated to a temperature at which boiling occurs. The distillation system is brought to equilibrium and the distillation commences with a chosen reflux ratio. The fractions obtained from the distillation are removed from the distillation apparatus. The amount of the desired fraction may be calculated by determining the proportion of sulfides. The desired fraction is obtained by maintaining accurate temperature control on the distillation system. The boiling fractions are removed at a specific vapor and temperature for that fraction. The reflux ratio is adjusted to maintain the temperature at which this fraction boils. After removal of the desired fraction, the fraction may be further filtered as desired.

In general, fractionation is carried out in a continuous or a batch process. In a continuous process, the material to be fractionated is fed to a fractionating column. Parameters are controlled in the system, such as feed flow, temperatures throughout the column, and the reflux ratio, etc., to separate the components in the feed into an overhead and bottoms stream. These parameters are adjusted to maintain the desired composition in the overhead and bottoms streams.

For a batch process, the material to be fractionated is charged to a vessel and is heated to boiling temperatures with agitation. Once the material reaches the boiling point, the fractionation column system is brought to equilibrium.

Subsequently, the desired reflux ratio is set. Collection of the distillate is commenced, as described herein. The reflux ratio is increased as is necessary to maintain the appropriate temperatures in the fractionating column system. As the distillation rate slows, the reflux ratio is increased until eventually the collection of the distillate stops. The different fractions are separated as the above process is repeated at higher temperatures.

The following examples relate to sulfurized olefins. Unless the context clearly indicates otherwise, here, as well as throughout the specification and claims, the amounts are by weight, the temperature is in degrees Celsius and the pressure is atmospheric.

Example S-1

Sulfur (526 parts, 16.4 moles) is charged to a jacketed, high-pressure reactor which is fitted with an agitator and internal cooling coils. Refrigerated brine is circulated through the coils to cool the reactor prior to the introduction of the gaseous reactants. After sealing the reactor, evacuating to about 2 torr and cooling, 920 parts (16.4 moles) of isobutene and 279 parts (8.2 moles) of hydrogen sulfide are charged to the reactor. The reactor is heated using steam in the external jacket, to a temperature of about 182°C over about 1.5 hours. A maximum pressure of 1350 psig is reached at about 168°C during this heat-up. Prior to reaching the peak reaction temperature, the pressure starts to decrease and continues to decrease steadily as the gaseous reactants are consumed. After about 10 hours at a reaction temperature of about 182°C, the pressure is 310-340 psig and the rate of pressure change is about 5-10 psig per hour. The unreacted hydrogen sulfide and isobutene are vented to a recovery system. After the pressure in the reactor has decreased to atmospheric, the sulfurized mixture is recovered as a liquid. The mixture is blown with nitrogen at about 100°C to remove low boiling materials including unreacted

isobutene, mercaptans and monosulfides. The residue after nitrogen blowing is agitated with 5% Super Filtrol and filtered, using a diatomaceous earth filter aid. The filtrate is the desired sulfurized composition which contains 42.5% sulfur.

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Example S-2

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Sulfur monochloride (2025 grams, 15.0 moles) is heated to 45°C. Through a sub-surface gas sparge, 1468 grams (26.2 moles) of isobutylene gas are fed into the reactor over a 5-hour period. The temperature is maintained between 45-50°C. At the end of the sparging, the reaction mixture increases in weight to 1352 grams. In a separate reaction vessel are added 2150 grams (16.5 moles) of 60% flake sodium sulfide, 240 grams (7.5 moles) sulfur, and a solution of 420 ml. of isopropanol in 4000 ml. of water. The contents are heated to 40°C. The adduct of the sulfur monochloride and isobutylene previously prepared is added over a three-quarter hour period while permitting the temperature to rise to 75°C. The reaction mixture is heated to reflux for 6 hours, and afterward the mixture is permitted to form into separate layers. The lower aqueous layer is discarded. The upper organic layer is mixed with two liters of 10% aqueous sodium hydroxide, and the mixture is heated to reflux for 6 hours. The organic layer is again removed and washed with one liter of water. The washed product is dried by heating at 90°C and 30 mm. Hg. pressure for 30 minutes. The residue is filtered through diatomaceous earth filter aid to give 2070 grams of a clear yellow-orange liquid.

Example S-3

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The product of Example S-1 (1000 lbs.) is charged to a reactor, under medium agitation, and heat to approximately 88°C - 94°C. The reaction mixture is brought to equilibrium and the equilibrium is maintained for 30 minutes prior to collection of distillate. The reflux ratio is set at 4:1. The temperature is raised to 105°C to ensure a steady distillation rate. Distillation is continued for approximately 20-24 hours and yields approximately 230-260 lbs. The temperature is raised to

105°C - 107°C. The system is brought to equilibrium and the equilibrium is maintained for 30 minutes prior to collection of distillate. The reflux ratio is set at 4:1. The temperature is raised to 121°C - 124°C, in order to ensure a steady distillation rate. The distillate is collected over 75-100 hours. The distillation yields approximately 300-400 lbs. of the desired product. The desired product contains 2-5% S2, 91-95% S3, and 1-2% S4.

Example S-4

In a vessel with a fractionation column, the product of Example S-1 (10,000 grams) is brought to a boil, approximately 200°F, under medium agitation. The column is brought to equilibrium by regulating the vapor temperature. The equilibrium is maintained for 30 minutes prior to collection of distillate. The reflux ratio is set at 5:1. Under these conditions, the distillate is collected until the accumulation of distillate is less than 5 ml in 15 minutes. The distillate (100 ml, 88 grams) is collected at a vapor temperature of 56°C. The temperature of the vessel is raised 15°F. An additional aliquot of 50 grams of distillate is removed, at a vapor temperature of 58°C. Distillate (1863) is collected and is removed. The collection is continued as long as the distillate rate stays greater than 5 ml/ 15 minutes. If boiling drops off, the temperature of the vessel is raised 5.5°C. Collection of distillate is continued until the distillation rate is less than 5 ml/15 minutes. The distillate contains approximately 473 grams of desired product. For the final collection of distillate, the temperature of the vessel is raised 9°C to 116°C, not exceeding 121°C. Distillate (220 ml, 214 grams) is removed at a vapor temperature of 69°C. Collection of the remainder of the distillate (4114 grams) is continued until the distillation rate is less than 5 ml/15 minutes. A yield after fractionation should approximate 6777 grams of the desired product. The desired product contains approximately 2% S2, 95.6% S3, and 0.15% S4.

In another embodiment, the sulfur compound is a sulfurized terpene compound. The term "terpene compound" as used in the specification and claims

is intended to include the various terpene hydrocarbons, such as contained in turpentine, pine oil and dipentenes, and the various synthetic and naturally occurring oxygen-containing derivatives. Pine-oil derivatives, which are commercially available from Hercules Incorporated, include α -terpineol (a high purity tertiary terpene alcohol); and Terpineol 318 Prime (a mixture containing about 60-65% weight α -terpineol and 15-20% weight beta-terpineol); Yarmor 302; Herco pine oil; Yarmor 302W; Yarmor F; and Yarmor 60.

In another embodiment, the sulfur compound is a sulfurized Diels-Alder adduct. The sulfurized Diels-Alder adduct is prepared by reacting a sulfur source, such as elemental sulfur, sulfur halides and organic polysulfides, including dialkyl polysulfides with a Diels-Alder adduct. A Diels-Alder reaction involves the reaction of one or more of the above conjugated dienes with one or more ethylenically or acetylenically unsaturated compounds, these latter compounds being known as dienophiles.

Dienophiles include nitroalkenes; α , β -ethylenically unsaturated carboxylic esters, acids or amides; ethylenically unsaturated aldehydes and vinyl ketones. The unsaturated carboxylic esters, acids and amides are described above. Specific examples of dienophiles include 1-nitrobutene-1-alkylacrylates, acrylamide, N,N'-dibutylacrylamide, methacrylamide, crotonaldehyde; crotonic acid, dimethyl divinyl ketone, methyl vinyl ketone, propiolaldehyde, methyl ethynyl ketone, propiolic acid, propargylaldehyde, cyclopentenedione, 3-cyanocoumaran, etc.

The sulfurized Diels-Alder adducts are prepared by means known to those in the art. Generally, the molar ratio of sulfur source to Diels-Alder adduct is in a range of from about 0.75 to about 4, or from about 1 to about 3, or to about 2.5. An example of a useful sulfurized Diels-Alder adduct is a sulfurized Diels-Alder adduct of butadiene and butyl-acrylate. Sulfurized Diels-Alder adducts, their intermediate components and methods of preparing them are described in U.S. Patents

3,498,915, 4,582,618, and Re 27,331. These patents are hereby incorporated by reference for their disclosures of sulfurized Diels-Alder adducts, intermediate components and methods of making the same.

5 In another embodiment, the sulfur compound is a metal containing or ashless dithiocarbamate. The metal-containing dithiocarbamates are prepared reacting a dithiocarbamic acid with a metal base. The metal base may be any metal compound capable of forming a metal salt. Examples of metal bases include metal oxides, hydroxides, carbonates, borates, or the like. The metals of the metal base include Group IA, IIA, IB through VIIB, and VIII metals (CAS version of the Periodic
10 Table of the Elements). These metals include the alkali metals, alkaline earth metals, and transition metals. In one embodiment, the metal is a Group IIA metal, such as calcium or magnesium, a Group IB metal, such as copper, a Group IIB metal, such as zinc, or a Group VIIB metal, such as manganese. Preferably the metal is magnesium, calcium, copper, or zinc. Examples of metal compounds which
15 may be reacted with the phosphorus acid include zinc hydroxide, zinc oxide, copper hydroxide, copper oxide, etc. Examples of metal containing dithiocarbamates zinc diamyldithiocarbamate, zinc di(2-ethylhexyl) dithiocarbamate, magnesium dibutyldithiocarbamate, magnesium dioctyldithiocarbamate, sodium diamyldithiocarbamate, and sodium diisopropyl dithiocarbamates. The metal
20 dithiocarbamates and their preparation are described in U.S. Patent 4,612,129, which is incorporated by reference.

In another embodiment, the sulfur compound is an ashless dithiocarbamate. The ashless dithiocarbamate may be an amine salt of a dithiocarbamic acid and one or more of the amines described below. The dithiocarbamate compositions include
25 reaction products of a dithiocarbamic acids or salts and an unsaturated amide, carboxylic acid, anhydride, or ester, or ether, alkylene-coupled dithiocarbamate, bis(S-alkyldithiocarbamoyl) disulfides and mixtures of two or more thereof. The dithiocarbamate compositions may also be prepared by simultaneously reacting an amine, carbon disulfide and an unsaturated compound. U.S. Patents 4,758,362

and 4,997,969 describe dithiocarbamate compositions and methods of making the same. These patents are hereby incorporated by reference for their disclosure of dithiocarbamate compositions and method of making the same.

5 The dithiocarbamic acid or salt used to prepare the dithiocarbamate compositions are prepared by reacting an amine with carbon disulfide. The amines may be primary or secondary amines, with secondary amines most preferred. The amines generally contain hydrocarbyl groups. Each hydrocarbyl group may independently contain from one to about 40, or from about two to about 30, or from three to about 24, or even to about 12 carbon atoms. Examples of groups, which
10 may be on the amines, include ethyl, propyl, butyl, hexyl, octyl and dodecyl groups.

In one embodiment, the amines are primary amines, including fatty primary amines, primary ether amines, and tertiary aliphatic amines. Examples of primary amines include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine. In one embodiment, the primary amine is a fatty
15 (C_{8-30}) amine, which include n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, oleyamine, etc. Other useful fatty amines include commercially available fatty amines, such as "Armeen" amines (products available from Akzo Chemicals, Chicago, Illinois). These amines include Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and
20 Armeen SD, wherein the letter designation relates to the fatty group, such as cocoa, oleyl, tallow, or stearyl groups.

Other useful primary amines include primary ether amines, such as those represented by the formula, $R''(OR')_xNH_2$, wherein R' is a divalent alkylene group having from about 2 to about 6 carbon atoms; x is a number from one to about 150,
25 or from one to about five, or one; and R'' is a hydrocarbyl group of about 5 to about 150, or from 6 to about 24 carbon atoms. An example of an ether amine is available under the name SURFAM® amines produced and marketed by Mars Chemical Company, Atlanta, Georgia. Preferred etheramines are exemplified by those identified as SURFAM P14B (decyloxypropylamine), SURFAM P16A (linear

C₁₆), SURFAM P17B (tridecyloxypropylamine). The carbon chain lengths (i.e., C₁₄, etc.) of the SURFAMS described above and used hereinafter are approximate and include the oxygen ether linkage.

In one embodiment, the amine is a tertiary-aliphatic primary amine. Generally, the aliphatic group, preferably an alkyl group, contains from about 4 to about 30, or from about 6 to about 24, or from about 8 to about 22 carbon atoms. Usually the tertiary aliphatic primary amines are monoamines represented by the formula $R_1-C(R_1')_2-NH_2$, wherein R_1 is a hydrocarbyl group containing from one to about 27 carbon atoms and R_1' is a hydrocarbyl group containing from 1 to about 12 carbon atoms. Such amines are illustrated by tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, and tert-octacosanylamine.

Mixtures of tertiary-aliphatic primary amines are also useful for the purposes of this invention. Illustrative of amine mixtures of this type are "Primene 81R" which is a mixture of C₁₁-C₁₄ tertiary alkyl primary amines and "Primene JMT" which is a similar mixture of C₁₈-C₂₂ tertiary alkyl primary amines (both are available from Rohm and Haas Company). The tertiary alkyl primary amines and methods for their preparation are known to those of ordinary skill in the art. The tertiary alkyl primary amines and methods for their preparation are described in U.S. Patent 2,945,749 which is hereby incorporated by reference for its teaching in this regard.

In another embodiment, the amine is a secondary amine. Specific of secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methyl,ethylamine, ethyl,butylamine, ethyl,amylamine and the like. In one embodiment, the secondary amines may be cyclic amines, such as piperidine, piperazine, morpholine, etc.

In one embodiment, the dithiocarbamate compound is prepared by reacting one or more of dithiocarbamic acids or salts with unsaturated reagents, such as the above described unsaturated amides, unsaturated anhydrides, acids, or esters,

unsaturated ethers. The unsaturated ethers contain from 3 to about 30, or from about 4 to about 24 carbon atoms. The unsaturated ethers include methyl vinyl ether, propyl vinyl ether, 2-ethyl hexyl vinyl ether, etc.

5 In another embodiment, the dithiocarbamate compound is an alkylene-coupled dithiocarbamate. The alkylene-coupled dithiocarbamates may be prepared by the reaction of a salt of a dithiocarbamic acid, described above, with a suitable dihalogen containing hydrocarbon. U.S. Patent 3,876,550, issued to Holubec, describes alkylene dithiocarbamate compounds and their preparation, and U.S. Patents 1,726,647 and 1,736,429, issued to Cadwell, describe phenylmethylen
10 bis(dithiocarbamates) and methods of making the same. These patents are incorporated by reference for their teachings related to dithiocarbamate compounds and methods for preparing the same. In one embodiment, the alkylene-coupled dithiocarbamate is derived from di-n-butyl amine, carbon disulfide and methylene dichloride.

15 In another embodiment, the dithiocarbamate compound is a bis(S-alkyldithiocarbamoyl) disulfide. These materials have previously been referred to as sulfur-coupled dithiocarbamates. The disulfides are prepared by (A) reacting a sulfur halide with about a stoichiometric equivalent of (i) at least one olefinic hydrocarbon, or (ii) an aldehyde or ketone, at a temperature and for a period of time
20 sufficient to produce a di(halohydrocarbyl)sulfur intermediate or a dialdehyde or diketo sulfur intermediate, and (B) reacting the intermediate with a salt of a dithiocarbamate in an amount sufficient generally to replace both halo groups with the dithiocarbamate groups or to react with both carbonyl groups of the dialdehyde or diketone. The sulfur halide utilized in the first step (A) may be sulfur
25 monochloride (i.e., S_2Cl_2), sulfur dichloride, sulfur monobromide, sulfur dibromide, or mixtures of any of the above sulfur halides with elemental sulfur in varying amounts.

The olefin may be any of the olefins described herein. The aldehydes include acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, 2-ethyl-hexanal,

and cyclohexanecarboxaldehyde. Examples of ketones include dimethyl ketone, methyl ethyl ketone, diethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, etc.

5 The bis(S-alkyldithiocarbamoyl) disulfides also may be prepared by a process which comprises the steps of (A) reacting an olefinic hydrocarbon with a halogen to produce a halogen-containing intermediate, and (B) reacting said intermediate with an alkali metal sulfide and a salt of a dithiocarbamate in an amount sufficient to replace the halogen groups present partially with dithiocarbamate groups and/or partially with sulfide groups. The bis(S-alkyldithiocarbamoyl) disulfides are described in U.S. Patent 2,599,350, issued to Rudel et al and U.S. Patent 10 5,141,658, issued to DiBiase. These patents are incorporated by reference for their disclosure of bis(S-alkyldithiocarbamoyl) disulfide.

Phosphorus Compounds

15 The lubricating compositions, and concentrates may include a phosphorus compound as the antiwear and extreme pressure agent (C). Typically, the phosphorus containing antiwear or extreme pressure agent is present at a level from about 0.01% to about 10%, or from about 0.05% or to about 4%, or from about 0.08% to about 3%, or from 0.1% to about 2% by weight in the lubricating composition. The phosphorus compound is selected from the group consisting of a phosphoric acid ester or salt thereof, a metal dithiophosphate, a reaction product of a phosphite and sulfur or a source of sulfur, a phosphite, a reaction product of a phosphorus acid or anhydride and an unsaturated compound, and mixtures of two or more thereof.

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25 In one embodiment, the phosphorus compound is a phosphorus acid ester. The ester is prepared by reacting one or more phosphorus acids or anhydrides with at least one alcohol. The phosphorus acid or anhydride is generally an inorganic phosphorus reagent, such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetroxide, phosphorous acid, phosphoric acid, phosphorus halide, C₁₋₇

phosphorus esters, and phosphorus sulfides, which include phosphorus pentasulfide, phosphorus sesquisulfide, phosphorus heptasulfide and the like.

The alcohols generally contain from one to about 30, or from two to about 24, or from about 3 to about 12 carbon atoms. The alcohols include propyl, butyl, amyl, 2-ethylhexyl, hexyl, octyl, oleyl, and cresol alcohols. Examples of commercially available alcohols include Alfol 810 (a mixture of primarily straight chain, primary alcohols having from 8 to 10 carbon atoms); Alfol 1218 (a mixture of synthetic, primary, straight-chain alcohols containing 12 to 18 carbon atoms); Alfol 20+ alcohols (mixtures of C_{18} - C_{28} primary alcohols having mostly C_{20} alcohols as determined by GLC (gas-liquid-chromatography); and Alfol 22+ alcohols (C_{18} - C_{28} primary alcohols containing primarily C_{22} alcohols). Alfol alcohols are available from Continental Oil Company. Examples of a commercially available alcohol mixtures are Adol 60 (about 75% by weight of a straight chain C_{22} primary alcohol, about 15% of a C_{20} primary alcohol and about 8% of C_{18} and C_{24} alcohols) and Adol 320 (oleyl alcohol). The Adol alcohols are marketed by Ashland Chemical.

A variety of mixtures of monohydric fatty alcohols derived from naturally occurring triglycerides and ranging in chain length from C_8 to C_{18} are available from Procter & Gamble Company. These mixtures contain various amounts of fatty alcohols containing mainly 12, 14, 16, or 18 carbon atoms. For example, CO-1214 is a fatty alcohol mixture containing 0.5% of C_{10} alcohol, 66.0% of C_{12} alcohol, 26.0% of C_{14} alcohol and 6.5% of C_{16} alcohol.

Another group of commercially available mixtures include the "Neodol" products available from Shell Chemical Co. For example, Neodol 23 is a mixture of C_{12} and C_{13} alcohols; Neodol 25 is a mixture of C_{12} and C_{15} alcohols; and Neodol 45 is a mixture of C_{14} to C_{15} linear alcohols. Neodol 91 is a mixture of C_9 , C_{10} and C_{11} alcohols.

The alcohol may also be a fatty vicinal diol. Fatty vicinal diols include those

available from Ashland Oil under the general trade designation Adol 114 and Adol 158. The former is derived from a straight chain α -olefin fraction of C_{11} - C_{14} , and the latter is derived from a C_{15} - C_{18} α -olefin fraction.

5 In one embodiment, the phosphoric acid ester is prepared by reacting one or more of the above alcohols with one or more of the above phosphorus reagents. Examples of phosphorus acid esters include phosphoric acid di- and tri- esters prepared by reacting a phosphoric acid or anhydride with cresol alcohols, e.g. tricresylphosphate.

10 In one embodiment, the phosphorus compound is a phosphorus ester prepared by reacting one or more dithiophosphoric acid with an epoxide or a glycol. This reaction product may be used alone, or further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide is generally an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, styrene oxide, etc. Propylene
15 oxide is preferred. The glycols may be aliphatic glycols, having from 1 to about 12, or from about 2 to about 6, or from about 2 to about 3 carbon atoms, or aromatic glycols. Glycols include ethylene glycol, propylene glycol, catechol, resorcinol, and the like. The dithiophosphoric acids, glycols, epoxides, inorganic phosphorus reagents and methods of reacting the same are described in U.S. Patent 3,197,405
20 and U.S. Patent 3,544,465 which are incorporated herein by reference for their disclosure to these.

The following Examples P-1 and P-2 exemplify the preparation of useful phosphorus acid esters.

25 Example P-1

Phosphorus pentoxide (64 grams) is added at 58°C over a period of 45 minutes to 514 grams of hydroxypropyl O,O-di(4-methyl-2-pentyl)phosphorodithioate (prepared by reacting di(4-methyl-2-pentyl)-phosphorodithioic acid with 1.3 moles of propylene oxide at 25°C). The mixture is heated at 75°C for 2.5 hours,

mixed with a diatomaceous earth and filtered at 70°C. The filtrate contains 11.8% by weight phosphorus, 15.2% by weight sulfur, and has an acid number of 87 (bromophenol blue).

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Example P-2

A mixture of 667 grams of phosphorus pentoxide and the reaction product of 3514 grams of diisopropyl phosphorodithioic acid with 986 grams of propylene oxide at 50°C is heated at 85°C for 3 hours and filtered. The filtrate contains 15.3% by weight phosphorus, 19.6% by weight sulfur, and has an acid number of 126 (bromophenol blue).

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When the phosphorus acid esters are acidic, they may be used in lubricants or they may be reacted further with ammonia, an amine, or metal base to form the corresponding ammonium or metal salt. The salts may be formed separately and then the salt of the phosphorus acid ester is added to the lubricating or functional fluid composition. Alternatively, the salts may also be formed when the phosphorus acid ester is blended with other components to form the lubricating or functional fluid composition. The phosphorus acid ester could then form salts with basic materials which are in the lubricating composition or functional fluid composition such as basic nitrogen containing compounds (e.g., acylated amines) and overbased metal salts.

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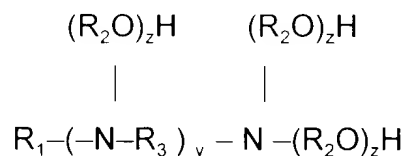
The ammonium salts of the phosphorus acid esters may be formed from ammonia, or an amine, or mixtures thereof. These amines can be monoamines or polyamines. Useful amines include those disclosed in U.S. Patent 4,234,435 at Col. 21, line 4 to Col. 27, line 50, this section of this reference being incorporated herein by reference. The monoamines generally have at least one hydrocarbyl group containing from 1 to about 24 carbon atoms, with from 1 to about 12 carbon atoms being preferred, with from 1 to about 6 being more preferred. Examples of monoamines primary amines and secondary amines described above. Tertiary amines include trimethylamine, tributylamine, methyldiethylamine, ethyldibutylamine, etc.

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In one embodiment, the amine may be a hydroxyamine. Typically, the hydroxyamines are primary, secondary or tertiary alkanol amines or mixtures thereof. Such amines can be represented by the formulae: $H_2-N-R'-OH$, $H(R'_1)N-R'-OH$, and $(R'_1)_2-N-R'-OH$, wherein each R'_1 is independently a hydrocarbyl group having from one to about eight carbon atoms or hydroxyhydrocarbyl group having from one to about eight carbon atoms, or from one to about four carbon atoms, and R' is a divalent hydrocarbyl group of about two to about 18 carbon atoms, or from two to about four carbon atoms. The group $-R'-OH$ in such formulae represents the hydroxyhydrocarbyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, propylene, 1,2-butene, 1,2-octadecene, etc. group. Where two R'_1 groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-member ring structure. Examples of such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like. Typically, however, each R'_1 is independently a methyl, ethyl, propyl, butyl, pentyl or hexyl group. Examples of these alkanolamines include mono-, di-, and triethanolamine, diethylethanolamine, ethylethanolamine, butyldiethanolamine, etc.

The hydroxyamines may also be an ether N-(hydroxyhydrocarbyl)amine. These are hydroxypoly(hydrocarbyloxy) analogs of the above-described hydroxyamines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyhydrocarbyl) amines can be conveniently prepared by reaction of one or more of the above epoxides with aforescribed amines and may be represented by the formulae: $H_2N-(R'O)_x-H$, $H(R'_1)N-(R'O)_x-H$, and $(R'_1)_2N-(R'O)_x-H$, wherein x is a number from about 2 to about 15 and R'_1 and R' are as described above. R'_1 may also be a hydroxypoly(hydrocarbyloxy) group.

In another embodiment, the amine is a hydroxyamine which may be represented by the formula



wherein R_1 is a hydrocarbyl group containing from about 6 to about 30 carbon atoms; R_2 is an alkylene group having from about two to about twelve carbon atoms, preferably an ethylene or propylene group; R_3 is an alkylene group containing from 1 to about 8, or from 1 to about 5 carbon atoms; y is zero or one; and each z is independently a number from zero to about 10, with the proviso that at least one z is zero.

Useful hydroxyhydrocarbyl amines where y in the above formula is zero include 2-hydroxyethyl hexylamine; 2-hydroxyethyloctylamine; 2-hydroxyethylpentadecylamine; 2-hydroxyethylolelamine; 2-hydroxyethylsoyamine; bis(2-hydroxyethyl)hexylamine; bis(2-hydroxyethyl)oleylamine; and mixtures thereof. Also included are the comparable members wherein in the above formula at least one z is at least 2, as for example, 2-hydroxyethoxyethylhexylamine.

In one embodiment, the amine may be a hydroxyhydrocarbyl amine, where referring to the above formula, y equals zero in the above formula. These hydroxyhydrocarbyl amines are available from the Akzo Chemical Division of Akzona, Inc., Chicago, Illinois, under the general trade designations "Ethomeen" and "Propomeen". Specific examples of such products include: Ethomeen C/15 which is an ethylene oxide condensate of a coconut fatty acid containing about 5 moles of ethylene oxide; Ethomeen C/20 and C/25 which are ethylene oxide condensation products from coconut fatty acid containing about 10 and 15 moles of ethylene oxide, respectively; Ethomeen O/12 which is an ethylene oxide condensation product of oleylamine containing about 2 moles of ethylene oxide per mole of amine; Ethomeen S/15 and S/20 which are ethylene oxide condensation

products with stearyl amine containing about 5 and 10 moles of ethylene oxide per mole of amine, respectively; Ethomeen T/12, T/15 and T/25 which are ethylene oxide condensation products of tallow amine containing about 2, 5 and 15 moles of ethylene oxide per mole of amine, respectively; and Propomeen O/12 which is the condensation product of one mole of oleyl amine with 2 moles propylene oxide.

The amine may also be a polyamine. The polyamines include alkoxyated diamines, fatty diamines, alkylenepolyamines, hydroxy containing polyamines, condensed polyamines, and heterocyclic polyamines. Commercially available examples of alkoxyated diamines include those amines where y in the above formula is one. Examples of these amines include Ethoduomeen T/13 and T/20 which are ethylene oxide condensation products of N-tallowtrimethylenediamine containing 3 and 10 moles of ethylene oxide per mole of diamine, respectively.

In another embodiment, the polyamine is a fatty diamine. The fatty diamines include mono- or dialkyl, symmetrical or asymmetrical ethylenediamines, propanediamines (1,2, or 1,3), and polyamine analogs of the above. Suitable commercial fatty polyamines are Duomeen C (N-coco-1,3-diaminopropane), Duomeen S (N-soya-1,3-diaminopropane), Duomeen T (N-tallow-1,3-diaminopropane), and Duomeen O (N-oleyl-1,3-diaminopropane). "Duomeens" are commercially available from Arma Chemical Co., Chicago, Illinois.

In another embodiment, the amine is an alkylenepolyamine. Alkylenepolyamines are represented by the formula $HR_1N-(\text{Alkylene-N})_n-(R_1)_2$, wherein each R_1 is independently hydrogen; or an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms; \bar{M}_n is a number from 1 to about 10, or from about 2 to about 7, or from about 2 to about 5; and the "Alkylene" group has from 1 to about 10 carbon atoms, or from about 2 to about 6, or from about 2 to about 4. In another embodiment, R_1 is defined the same as R'_1 above. Such alkylenepolyamines include methylenepolyamines, ethylenepolyamines, butylenepolyamines, propylenepolyamines, pentylenepolyamines, etc. The higher homologs and related heterocyclic amines, such as piperazines and N-amino

alkyl-substituted piperazines, are also included. Specific examples of such polyamines are ethylenediamine, triethylenetetramine, tris-(2-aminoethyl)amine, propylenediamine, trimethylenediamine, tripropylenetetramine, triethylenetetraamine, tetraethylenepentamine, hexaethyleneheptamine, pentaethylenehexamine, etc. Higher homologs obtained by condensing two or more of the above-noted alkyleneamines are similarly useful as are mixtures of two or more of the aforescribed polyamines.

In one embodiment, the polyamine is an ethylenepolyamine. Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology", 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Ethylenepolyamines are often a complex mixture of polyalkylenepolyamines including cyclic condensation products. Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave, as residue, what is often termed "polyamine bottoms". In general, alkylenepolyamine bottoms can be characterized as having less than 2%, usually less than 1% (by weight) material boiling below about 200°C. A typical sample of such ethylenepolyamine bottoms obtained from the Dow Chemical Company of Freeport, Texas designated "E-100" has a specific gravity at 15.6°C of 1.0168, a percent nitrogen by weight of 33.15 and a viscosity at 40°C of 121 centistokes. Gas chromatography analysis of such a sample contains about 0.93% "Light Ends" (most probably diethylenetriamine), 0.72% triethylenetetraamine, 21.74% tetraethylenepentaamine and 76.61% pentaethylenehexamine and higher analogs. These alkylenepolyamine bottoms include cyclic condensation products such as piperazine and higher analogs of diethylenetriamine, triethylenetetramine and the like. These alkylenepolyamine bottoms may be reacted alone or they may be used with other amines, polyamines, or mixtures thereof.

Another useful polyamine is a condensation reaction between at least one hydroxy compound with at least one polyamine reactant containing at least one

primary or secondary amino group. The hydroxy compounds are preferably polyhydric alcohols and amines. The polyhydric alcohols contain from 2 to about 40 carbon atoms, from 2 to about 20 carbon atoms; and from 2 to about 10 hydroxyl groups, or from 2 to about 6 hydroxyl groups. Polyhydric alcohols include ethylene glycols, including di-, tri- and tetraethylene glycols; propylene glycols, including di-, tri- and tetrapropylene glycols; glycerol; butanediol; hexanediol; sorbitol; arabitol; mannitol; trimethylolpropane; sucrose; fructose; glucose; cyclohexanediol; erythritol; and pentaerythritols, including di- and tripentaerythritol.

In one embodiment, the hydroxy compounds are polyhydric amines. Polyhydric amines include any of the above-described monoamines reacted with an alkylene oxide (e.g., ethylene oxide, propylene oxide, butylene oxide, etc.) having from two to about 20, or from two to about four carbon atoms. Examples of polyhydric amines include tris-(hydroxypropyl)amine, tris-(hydroxymethyl)aminomethane, 2-amino-2-methyl-1,3-propanediol, N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine, and N,N,N',N'-tetrakis (2-hydroxyethyl) ethylenediamine, preferably tris-(hydroxymethyl) aminomethane (THAM).

Polyamines which may react with the polyhydric alcohol or amine to form the condensation products or condensed amines, are described above. Preferred polyamines are polyalkylene polyamines such as triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenhexamine (PEHA), and mixtures of polyamines such as the above-described "amine bottoms". The amine condensates and methods of making the same are described in PCT publication WO 86/05501 and U.S. Patent 5,230,714 (Steckel) which are incorporated by reference for its disclosure to the condensates and methods of making. A particularly useful amine condensate is prepared from HPA Taft Amines, amine bottoms, available commercially from Union Carbide Co., and tris(hydroxymethyl)aminomethane (THAM).

In another embodiment, the polyamines are polyoxyalkylene polyamines, e.g. polyoxyalkylene diamines and polyoxyalkylene triamines, having average molecular

weights ranging from about 200 to about 4000, or from about 400 to about 2000. The preferred polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403, etc.". U.S. Patents 3,804,763 and 3,948,800 are expressly incorporated herein by reference for their disclosure of such polyoxyalkylene polyamines and acylated products made therefrom.

In another embodiment, the polyamines are hydroxy-containing polyamines. Hydroxy-containing polyamine analogs of hydroxy monoamines, particularly alkoxy-ated alkylene polyamines, e.g., N,N-(diethanol)ethylenediamines can also be used. Such polyamines can be made by reacting the above-described alkylene amines with one or more of the above-described alkylene oxides. Similar alkylene oxide-alkanol amine reaction products may also be used such as the products made by reacting the above described primary, secondary or tertiary alkanol amines with ethylene, propylene or higher epoxides in a 1.1 to 1.2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art. Specific examples of hydroxy-containing polyamines include N-(2-hydroxyethyl) ethylenediamine, N,N'-bis(2-hydroxyethyl)-ethylenediamine, 1-(2-hydroxyethyl)-piperazine, mono(hydroxypropyl)-substituted tetraethylenepentamine, N-(3-hydroxybutyl)-tetramethylenediamine, etc. Higher homologs obtained by condensation of the above illustrated hydroxy-containing polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the above described polyamines are also useful.

In another embodiment, the amine is a heterocyclic amine. The heterocyclic polyamines include aziridines, azetidines, azolidines, tetra- and dihydropyridines,

pyrroles, indoles, piperidines, imidazoles, di- and tetrahydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkylpiperazines, N,N'-di-aminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Preferred heterocyclic amines are the saturated 5- and 6-member heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl substituted piperidines, piperazine, aminoalkyl substituted piperazines, morpholine, aminoalkyl substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially preferred. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminoethylpiperazine, and N,N'-diaminoethylpiperazine. Hydroxy heterocyclic amines are also useful. Examples include N-(2-hydroxyethyl)cyclohexylamine, 3-hydroxycyclopentylamine, parahydroxyaniline, N-hydroxyethylpiperazine, and the like.

In another embodiment, the phosphorus acid ester or salt is a metal salt. The metal salts of the phosphorus acid esters are prepared by the reaction of one or more of the above metal bases with an phosphorus acid ester.

In another embodiment, the phosphorus compound is a metal thiophosphate, preferably a metal dithiophosphate. The metal thiophosphates are prepared by reacting a metal base with one or more thiophosphorus acids. The thiophosphorus acid may be mono- or dithiophosphorus acids. The thiophosphorus acid may be prepared by reacting one or more of the above phosphorus sulfides with one or more of the above alcohols.

Thiophosphoric acids, such as a monothiophosphorus acid, may be prepared by the reaction of a sulfur source with a dihydrocarbyl phosphite. The sulfur source may for instance be elemental sulfur, or a sulfide, such as a sulfurized olefin. Elemental

sulfur is a preferred sulfur source. The preparation of monothiophosphoric acids are disclosed in U.S. Patent 4,755,311 and PCT Publication WO 87/07638, which are incorporated herein by reference for their disclosure of monothiophosphoric acids, sulfur sources, and the process for making monothiophosphoric acids.

5 Monothiophosphoric acids may also be formed in the lubricant blend by adding a dihydrocarbyl phosphite to a lubricating composition containing a sulfur source, such as elemental, sulfur, the combination of sulfur and hydrogen sulfide and a sulfurized olefin, such as those described above. The phosphite may react with the sulfur source under blending conditions (i.e., temperatures from about 30°C to

10 about 100°C, or higher) to form the monothiophosphoric acid.

In another embodiment, the phosphorus acid is a dithiophosphoric acid or phosphorodithioic acid. The dithiophosphoric acid may be represented by the formula $(R_1O)_2PSSH$, wherein each R_1 is independently a hydrocarbyl group, containing from about 3 to about 30, or from about 3 to about 18, or from about 4

15 to about 12, or to about 8 carbon atoms. Examples R_1 include isopropyl, isobutyl, n-butyl, sec-butyl, amyl, n-hexyl, methylisobutyl carbanyl, heptyl, 2-ethylhexyl, isooctyl, nonyl, behenyl, decyl, dodecyl, tridecyl, alkylphenyl groups, or mixtures thereof. Illustrative lower alkylphenyl R_1 groups include butylphenyl, amylphenyl, and heptylphenyl and mixtures thereof. Examples of mixtures of R_1 groups include:

20 1-butyl and 1-octyl; 1-pentyl and 2-ethyl-1-hexyl; isobutyl and n-hexyl; isobutyl and isoamyl; 2-propyl and 2-methyl-4-pentyl; isopropyl and sec-butyl; and isopropyl and isooctyl.

Examples of metal dithiophosphates include zinc isopropyl, methylamyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, barium di(nonyl) dithio-

25 phosphate, zinc di(cyclohexyl) dithiophosphate, copper di(isobutyl) dithiophosphate, calcium di(hexyl) dithiophosphate, zinc isobutyl isoamyl dithiophosphate, and zinc isopropyl secondary-butyl dithiophosphate. In another embodiment, the metal dithiophosphates are further reacted with one or more of the above described epoxides, preferably propylene oxide. These reaction products are described in

U.S. Patent 3,213,020; 3,213,021; and 3,213,022, issued to Hopkins et al. These patents are incorporated by reference for such description of the reaction products.

The following Examples P-3 to P-7 exemplify the preparation of useful phosphorus acid ester salts.

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Example P-3

A reaction vessel is charged with 217 grams of the filtrate from Example P-1. A commercial aliphatic primary amine (66 grams), having an average molecular weight of 191 in which the aliphatic radical is a mixture of tertiary alkyl radicals containing from 11 to 14 carbon atoms, is added over a period of 20 minutes at 25-60°C. The resulting product has a phosphorus content of 10.2% by weight, a nitrogen content of 1.5% by weight, and an acid number of 26.3.

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Example P-4

The filtrate of Example P-2 (1752 grams) is mixed at 25-82°C with 764 grams of the aliphatic primary amine used in of Example P-3. The resulting product has 9.95% phosphorus, 2.72% nitrogen, and 12.6% sulfur.

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Example P-5

Alfol 8-10 (2628 parts, 18 moles) is heated to a temperature of about 45°C whereupon 852 parts (6 moles) of phosphorus pentoxide are added over a period of 45 minutes while maintaining the reaction temperature between about 45-65°C. The mixture is stirred an additional 0.5 hour at this temperature, and is there- after heated at 70°C for about 2-3 hours. Primene 81-R (2362 parts, 12.6 moles) is added dropwise to the reaction mixture while maintaining the temperature between about 30-50°C. When all of the amine has been added, the reaction mixture is filtered through a filter aid, and the filtrate is the desired amine salt containing 7.4% phosphorus (theory, 7.1%).

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Example P-6

Phosphorus pentoxide (852 grams) is added to 2340 grams of iso-octyl alcohol over a period of 3 hours. The temperature increases from room temperature but is maintained below 65°C. After the addition is complete the reaction mixture is heated to 90°C and the temperature is maintained for 3 hours. Diatomaceous earth is added to the mixture, and the mixture is filtered. The filtrate has 12.4% phosphorus, a 192 acid neutralization number (bromophenol blue) and a 290 acid neutralization number (phenolphthalein).

The above filtrate is mixed with 200 grams of toluene, 130 grams of mineral oil, 1 gram of acetic acid, 10 grams of water and 45 grams of zinc oxide. The mixture is heated to 60-70°C under a pressure of 30 mm Hg. The resulting product mixture is filtered using a diatomaceous earth. The filtrate has 8.58% zinc and 7.03% phosphorus.

Example P-7

Phosphorus pentoxide (208 grams) is added to the product prepared by reacting 280 grams of propylene oxide with 1184 grams of O,O'-diisobutylphosphorodithioic acid at 30-60°C. The addition is made at a temperature of 50-60°C and the resulting mixture is then heated to 80°C and held at that temperature for 2 hours. The commercial aliphatic primary amine identified in Example P-3 (384 grams) is added to the mixture, while the temperature is maintained in the range of 30-60°C. The reaction mixture is filtered through diatomaceous earth. The filtrate has 9.31% phosphorus, 11.37% sulfur, 2.50% nitrogen, and a base number of 6.9 (bromophenol blue indicator).

In another embodiment, phosphorus compound is a metal salt of (a) at least one dithiophosphoric acid and (b) at least one aliphatic or alicyclic carboxylic acid. The dithiophosphoric acids are described above. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3, or just one carboxylic acid group. The preferred carboxylic acids are those having the

formula RCOOH, wherein R is a hydrocarbyl group, preferably free from acetylenic unsaturation. Generally, R contains from about 2 to about 40, or from about 3 to about 24, or from about 4 to about 12 carbon atoms. In one embodiment, R contains from about 4 to about 12, or from about 8 to about 12, or to about 8 carbon atoms. In one embodiment, R is an alkyl group. Suitable acids include the butanoic, pentanoic, hexanoic, octanoic, nonanoic, decanoic, dodecanoic, octodecanoic and eicosanoic acids, as well as olefinic acids such as oleic, linoleic, and linolenic acids, and linoleic dimer acid. A preferred carboxylic acid is 2-ethylhexanoic acid.

The metal salts may be prepared by merely blending a metal salt of a dithiophosphoric acid with a metal salt of a carboxylic acid in the desired ratio. The ratio of equivalents of dithiophosphoric acid to carboxylic acid is from about 0.5 to about 400 to 1. The ratio may be from 0.5 to about 200, or to about 100, or to about 50, or to about 20 to 1. In one embodiment, the ratio is from 0.5 to about 4.5 to 1, or from about 2.5 to about 4.25 to 1. For this purpose, the equivalent weight of a dithiophosphoric acid is its molecular weight divided by the number of -PSSH groups therein, and the equivalent weight of a carboxylic acid is its molecular weight divided by the number of carboxy groups therein.

A second method for preparing the metal salts is to prepare a mixture of the acids in the desired ratio, such as those described above for the metal salts of the individual metal salts, and to react the acid mixture with one of the above described metal compounds. When this method of preparation is used, it is frequently possible to prepare a salt containing an excess of metal with respect to the number of equivalents of acid present; thus the metal salts may contain as many as 2 equivalents and especially to about 1.5 equivalents of metal per equivalent of acid may be prepared. The equivalent of a metal for this purpose is its atomic weight divided by its valence. U.S. Patents 4,308,154 and 4,417,990 describe procedures for preparing these metal salts and disclose a number of examples of such metal salts. These patents are hereby incorporated by reference for those disclosures.

In another embodiment, the phosphorus compound may be a phosphite. In one embodiment, the phosphite is a di- or trihydrocarbyl phosphite. Preferably each hydrocarbyl group has from 1 to about 24 carbon atoms, or from 1 to about 18 carbon atoms, or from about 2 to about 8 carbon atoms. Each hydrocarbyl group may be independently alkyl, alkenyl, aryl, and mixtures thereof. When the hydrocarbyl group is an aryl group, then it contains at least about 6 carbon atoms; or from about 6 to about 18 carbon atoms. Examples of the alkyl or alkenyl groups include propyl, butyl, hexyl, heptyl, octyl, oleyl, linoleyl, stearyl, etc. Examples of aryl groups include phenyl, naphthyl, heptylphenol, etc. Preferably each hydrocarbyl group is independently propyl, butyl, pentyl, hexyl, heptyl, oleyl or phenyl, more preferably butyl, oleyl or phenyl and more preferably butyl, oleyl, or phenyl. Phosphites and their preparation are known and many phosphites are available commercially. Particularly useful phosphites are dibutyl hydrogen phosphite, dioleyl hydrogen phosphite, di(C₁₄₋₁₈) hydrogen phosphite, and triphenyl phosphite.

In one embodiment, the phosphorus compound may be a reaction product of a phosphorus acid and an unsaturated compound. The unsaturated compounds include above described unsaturated amides, esters, acids, anhydrides, and ethers. The phosphorus acids are described above, preferably the phosphorus acid is a dithiophosphoric acid.

Boron-Containing Antiwear/Extreme Pressure Agents

The lubricants and/or functional fluids may additionally contain a boron compound, as the antiwear or extreme pressure agent (C). In one embodiment, the boron containing antiwear/extreme pressure agent is present in the lubricants and functional fluids at a level from about 0.08% to about 4%, or from 0.1% to about 3% by weight. Examples of boron containing antiwear/extreme pressure agents include a borated dispersant; an alkali metal or a mixed alkali metal, alkaline earth metal borate; a borated overbased metal salt; a borated epoxide; and a borate ester.

In one embodiment, the boron compound is a borated dispersant. Typically, the borated dispersant contains from about 0.1% to about 5%, or from about 0.5% to about 4%, or from 0.7% to about 3% by weight boron. In one embodiment, the borated dispersant is a borated acylated amine, such as a borated succinimide dispersant. Borated dispersants are described in 3,000,916; 3,087,936; 3,254,025; 3,282,955; 3,313,727; 3,491,025; 3,533,945; 3,666,662 and 4,925,983. These references are incorporated by reference for their disclosure of borated dispersants. Borated dispersant are prepared by reaction of one or more dispersant with one or more boron compounds. The dispersants include acylated amines, carboxylic esters, Mannich reaction products, hydrocarbyl substituted amines, and mixtures thereof.

The acylated amines include reaction products of one or more carboxylic acylating agent and one or more amine. The carboxylic acylating agents include C_8 fatty acids, C_{14-20} isoaliphatic acids, C_{18-44} dimer acids, addition dicarboxylic acids, trimer acids, addition tricarboxylic acids, and hydrocarbyl substituted carboxylic acylating agents. Dimer acids are described in U.S. Patents 2,482,760, 2,482,761, 2,731,481, 2,793,219, 2,964,545, 2,978,468, 3,157,681, and 3,256,304, the entire disclosures of which are incorporated herein by reference. The addition carboxylic acylating agents are addition (4+2 and 2+2) products of an unsaturated fatty acid with one or more unsaturated carboxylic reagents, which are described above. These acids are taught in U.S. Patent No. 2,444,328, the disclosure of which is incorporated herein by reference. In another embodiment, the carboxylic acylating agent is a hydrocarbyl substituted carboxylic acylating agent. The hydrocarbyl substituted carboxylic acylating agents are prepared by a reaction of one or more of the above olefins or polyalkenes with one or more of the above unsaturated carboxylic reagent, such as maleic anhydride. The amines may be any of those described above, preferably a polyamine, such as an alkylenepolyamine or a condensed polyamine. Acylated amines, their intermediates and methods for preparing the same are described in U.S. Patents 3,219,666; 4,234,435; 4,952,328;

4,938,881; 4,957,649; 4,904,401; and 5,053,152. Those patents are hereby incorporated by reference for such disclosure.

5 In another embodiment, the dispersant may also be a carboxylic ester. The carboxylic ester is prepared by reacting at least one or more of the above carboxylic acylating agents, preferably a hydrocarbonyl substituted carboxylic acylating agent, with at least one organic hydroxy compound and optionally an amine. The hydroxy compound may be an alcohol or a hydroxy containing amine. In another embodiment, the carboxylic ester dispersant is prepared by reacting the acylating agent with at least one of the above-described hydroxyamines. The alcohols are described above. Preferred alcohols are the above polyhydric alcohols, such as pentaerythritol.

10 The polyhydric alcohols may be esterified with monocarboxylic acids having from 2 to about 30, or from about 8 to about 18 carbon atoms, provided that at least one hydroxyl group remains unesterified. Examples of monocarboxylic acids include acetic, propionic, butyric and above described fatty acids. Specific examples of these esterified polyhydric alcohols include sorbitol oleate, including mono- and dioleate, sorbitol stearate, including mono- and distearate, glycerol oleate, including glycerol mono-, di- and trioleate and erythritol octanoate.

15 The carboxylic ester dispersants may be prepared by any of several known methods. The method which is preferred because of convenience and the superior properties of the esters it produces, involves the reaction of the carboxylic acylating agents described above with one or more alcohol or phenol in ratios from about 0.5 equivalent to about 4 equivalents of hydroxy compound per equivalent of acylating agent. The preparation of useful carboxylic ester dispersant is described in U.S. Patents 3,522,179 and 4,234,435, and their disclosures are incorporated by reference.

20 The carboxylic ester dispersants may be further reacted with at least one of the above described amines, such as a polyethylenepolyamine, condensed polyamine, or a heterocyclic amine, such as aminopropylmopholine. The amine is

added in an amount sufficient to neutralize any non-esterified carboxyl groups. In one embodiment, the carboxylic ester dispersants are prepared by reacting from about 1 to about 2 equivalents, or from about 1.0 to 1.8 equivalents of hydroxy compounds, and up to about 0.3 equivalent, or from about 0.02 to about 0.25 equivalent of polyamine per equivalent of acylating agent. The carboxylic acid acylating agent may be reacted simultaneously with both the hydroxy compound and the amine. There is generally at least about 0.01 equivalent of the alcohol and at least 0.01 equivalent of the amine although the total amount of equivalents of the combination should be at least about 0.5 equivalent per equivalent of acylating agent. These carboxylic ester dispersant compositions are known in the art, and the preparation of a number of these derivatives is described in, for example, U.S. Patents 3,957,854 and 4,234,435 which have been incorporated by reference previously.

In another embodiment, the dispersant may also be a hydrocarbyl-substituted amine. These hydrocarbyl-substituted amines are well known to those skilled in the art. These amines are disclosed in U.S. Patents 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,755,433; and 3,822,289. These patents are hereby incorporated by reference for their disclosure of hydrocarbyl amines and methods of making the same. Typically, hydrocarbyl substituted amines are prepared by reacting olefins and olefin polymers, including the above polyalkenes and halogenated derivatives thereof, with amines (mono- or polyamines). The amines may be any of the amines described above, preferably an alkylene polyamine. Examples of hydrocarbyl substituted amines include poly(propylene)amine; N,N-dimethyl-N-poly(ethylene/propylene)amine, (50:50 mole ratio of monomers); polybutene amine; N,N-di(hydroxyethyl)-N-polybutene amine; N-(2-hydroxypropyl)-N-polybutene amine; N-polybutene-aniline; N-polybutenemorpholine; N-poly(butene)ethylenediamine; N-poly(propylene)trimethylenediamine; N-poly(butene)diethylenetriamine; N',N'-poly(butene)tetraethylenepentamine; N,N-dimethyl-N'-poly(propylene)-1,3-propylenediamine and the like.

In another embodiment, the dispersant may also be a Mannich dispersant. Mannich dispersants are generally formed by the reaction of at least one aldehyde, such as formaldehyde and paraformaldehyde, at least one of the above described amines, preferably a polyamine, such as a polyalkylenepolyamine, and at least one alkyl substituted hydroxyaromatic compound. The amounts of the reagents is such that the molar ratio of hydroxyaromatic compound to formaldehyde to amine is in the range from about (1:1:1) to about (1:3:3). The hydroxyaromatic compound is generally an alkyl substituted hydroxyaromatic compound. This term includes the above described phenols. The hydroxyaromatic compounds are those substituted with at least one, and preferably not more than two, aliphatic or alicyclic groups having from about 6 to about 400, or from about 30 to about 300, or from about 50 to about 200 carbon atoms. These groups may be derived from one or more of the above described olefins or polyalkenes. In one embodiment, the hydroxyaromatic compound is a phenol substituted with an aliphatic or alicyclic hydrocarbon-based group having an \bar{M}_n of about 420 to about 10,000. Mannich dispersants are described in the following patents: U.S. Patent 3,980,569; U.S. Patent 3,877,899; and U.S. Patent 4,454,059 (herein incorporated by reference for their disclosure to Mannich dispersants).

In one embodiment, the boron compound is an alkali or mixed alkali metal and alkaline earth metal borate. These metal borates are generally a hydrated particulate metal borate which are known in the art. Alkali metal borates include mixed alkali and alkaline metal borates. These metal borates are available commercially. Representative patents disclosing suitable alkali and alkali metal and alkaline earth metal borates and their methods of manufacture include U.S. 3,997,454; 3,819,521; 3,853,772; 3,907,601; 3,997,454; and 4,089,790. These patents are incorporated by reference for their disclosures of the metal borates and methods of their manufacture.

In another embodiment, the boron compound is a borated fatty amine. The borated amines are prepared by reacting one or more of the above boron

compounds with one or more of the above fatty amines, e.g., an amine having from about four to about eighteen carbon atoms. The borated fatty amines are prepared by reacting the amine with the boron compound from about 50°C to about 300°C, or from about 100°C to about 250°C, and at a ratio from about 3:1 to about 1:3 equivalents of amine to equivalents of boron compound.

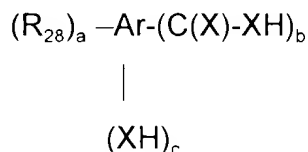
In another embodiment, the boron compound is an overbased metal salt and is present in an amount from about 0.5% to about 4%, or from about 0.7% to about 3%, or from about 0.9% to about 2% by weight of the lubricating composition. Overbased metal salts are characterized by having a metal content in excess of that which would be present according to the stoichiometry of the metal and the acidic organic compound. The amount of excess metal is commonly expressed in metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A salt having a metal ratio of 4.5 will have 3.5 equivalents of excess metal. The overbased salts generally have a metal ratio from about 1.5 up to about 40, or from about 2 up to about 30, or from about 3 up to about 25. In one embodiment, the metal ratio is greater than about 7, or greater than about 10, or greater than about 15.

The overbased materials are prepared by reacting an acidic material, typically carbon dioxide, with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent for the acidic organic compound, a stoichiometric excess of a basic metal compound, and a promoter. Generally, the basic metal compounds are oxides, hydroxides, chlorides, carbonates, and phosphorus acids (phosphonic or phosphoric acid) salts, and sulfur acid (sulfuric or sulfonic) salts. The metals of the basic metal compounds are generally alkali, alkaline earth, and transition metals. Examples of the metals of the basic metal compound include sodium, potassium, lithium, magnesium, calcium, barium, titanium, manganese, cobalt, nickel, copper, zinc, and preferably sodium, potassium, calcium, and magnesium.

The acidic organic compounds useful in making the overbased compositions of the present invention include carboxylic acylating agents, sulfonic acids, phosphorus containing acids, phenols, or mixtures of two or more thereof. Preferably, the acidic organic compounds are carboxylic acylating agents, or sulfonic acids. In one embodiment, the acidic organic compounds is one or more of the above described carboxylic acylating agent, such as a hydrocarbyl substituted carboxylic acylating agents, such as the hydrocarbyl substituted succinic anhydrides.

In another embodiment, the carboxylic acylating agent is an alkylalkyleneglycol-acetic acid, or alkylpolyethyleneglycol-acetic acid. Some specific examples of these compounds include: iso-stearyl-pentaethyleneglycol-acetic acid; iso-stearyl-O-(CH₂CH₂O)₅CH₂CO₂Na; lauryl-O-(CH₂CH₂O)_{2.5}CH₂CO₂H; lauryl-O-(CH₂CH₂O)_{3.5}CH₂CO₂H; oleyl-O-(CH₂CH₂O)₄CH₂CO₂H; lauryl-O-(CH₂CH₂O)_{4.5}CH₂CO₂H; lauryl-O-(CH₂CH₂O)₁₆CH₂CO₂H; octyl-phenyl-O-(CH₂CH₂O)₆CH₂CO₂H; octyl-phenyl-O-(CH₂CH₂O)₁₉CH₂CO₂H; 2-octyl-decanyl-O-(CH₂CH₂O)₆CH₂CO₂H. These acids are available commercially from Sandoz Chemical Co. under the tradename of Sandopan acids.

In another embodiment, the carboxylic acylating agents are aromatic carboxylic acids. A group of useful aromatic carboxylic acids are those of the formula

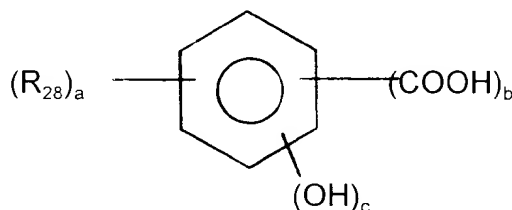


wherein R₂₈ is an aliphatic hydrocarbyl group having from about 4 to about 400 carbon atoms, a is a number in the range of zero to about 4, Ar is an aromatic group, such as those discussed above, each X is independently sulfur or oxygen,

preferably oxygen, b is a number in the range from one to about four, c is a number in the range of zero to about four, usually one or two, with the proviso that the sum of a, b and c does not exceed the number of valences of Ar. In one embodiment, R_{28} and a are such that there is an average of at least about eight aliphatic carbon atoms provided by the R_{28} groups.

The R_{28} group is a hydrocarbyl group that is directly bonded to the aromatic group Ar. R_{28} typically contains from about 6 to about 80, or from about 7 to about 30, or from about 8 to about 25, or from about 8 to about 15 carbon atoms. Examples of R_{28} groups include butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, 5-chlorohexyl, 4-ethoxypentyl, 3-cyclohexyloctyl, 2,3,5-trimethylheptyl, propylene tetramer, triisobutenyl and substituents derived from one of the above described olefins or polyalkenes.

Within this group of aromatic acids, a useful class of carboxylic acids are those of the formula



wherein R_{28} is defined above, a is a number in the range of from zero to about 4, or from 1 to about 3; b is a number in the range of 1 to about 4, or from 1 to about 2, c is a number in the range of zero to about 4, or from 1 to about 2, and or 1; with the proviso that the sum of a, b and c does not exceed 6. In one embodiment, R_{28} and a are such that the acid molecules contain at least an average of about 12 aliphatic carbon atoms in the aliphatic hydrocarbon substituents per acid molecule. Typically, b and c are each one and the carboxylic acid is a salicylic acid.

In one embodiment, the salicylic acids are hydrocarbyl substituted salicylic acids, wherein each hydrocarbyl substituent contains an average of at least about

8 carbon atoms per substituent and 1 to 3 substituents per molecule. In one embodiment, the hydrocarbyl substituent is derived from one or more above-described polyalkenes.

5 The above aromatic carboxylic acids are well known or can be prepared according to procedures known in the art. Carboxylic acids of the type illustrated by these formulae and processes for preparing their neutral and basic metal salts are well known and disclosed, for example, in U.S. Patents 2,197,832; 2,197,835; 2,252,662; 2,252,664; 2,714,092; 3,410,798; and 3,595,791.

10 In another embodiment, the acidic organic compound is a sulfonic acid. The sulfonic acids include sulfonic and thiosulfonic acids, preferably sulfonic acids. The sulfonic acids include the mono- or polynuclear aromatic or cycloaliphatic compounds. The oil-soluble sulfonic acids may be represented for the most part by one of the following formulae: $R_{29}-T-(SO_3)_aH$ and $R_{30}-(SO_3)_bH$, wherein T is a cyclic nucleus such as benzene, naphthalene, anthracene, diphenylene oxide, 15 diphenylene sulfide, and petroleum naphthenes; R_{29} is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, etc.; $(R_{29})+T$ contains a total of at least about 15 carbon atoms; and R_{30} is an aliphatic hydrocarbyl group containing at least about 15 carbon atoms. Examples of R_{30} are alkyl, alkenyl, alkoxyalkyl, carboalkoxyalkyl, etc. Specific examples of R_{30} are groups derived from petrolatum, saturated and 20 unsaturated paraffin wax, and one or more of the above-described polyalkenes. The groups T, R_{29} , and R_{30} in the above Formulae can also contain other inorganic or organic substituents in addition to those enumerated above such as, for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, disulfide, etc. In the above Formulae, a and b are at least 1.

25 A preferred group of sulfonic acids are mono-, di-, and tri-alkylated benzene and naphthalene sulfonic acids including their hydrogenated forms. Illustrative of synthetically produced alkylated benzene and naphthalene sulfonic acids are those containing alkyl substituents having from about 8 to about 30 carbon atoms, or from about 12 to about 30 carbon atoms, and or to about 24 carbon atoms. Specific

examples of sulfonic acids are mahogany sulfonic acids; bright stock sulfonic acids; sulfonic acids derived from lubricating oil fractions having a Saybolt viscosity from about 100 seconds at 100°F to about 200 seconds at 210°F; petrolatum sulfonic acids; mono- and polywax-substituted sulfonic acids; alkylbenzene sulfonic acids (where the alkyl group has at least 8 carbons), dilaurylbeta-naphthyl sulfonic acids, and alkaryl sulfonic acids, such as dodecylbenzene "bottoms" sulfonic acids.

Dodecylbenzene "bottoms" sulfonic acids are the material leftover after the removal of dodecylbenzene sulfonic acids that are used for household detergents. The "bottoms" may be straight-chain or branched-chain alkylates with a straight-chain dialkylate preferred. The production of sulfonates from detergent manufactured by-products by reaction with, e.g., SO_3 , is well known to those skilled in the art. See, for example, the article "Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology", Second Edition, Vol. 19, pp. 291 et seq. published by John Wiley & Sons, N.Y. (1969).

In another embodiment, the acidic organic compound is a phosphorus containing acid. The phosphorus containing acids are one or more of the above described phosphorus containing acids. In one embodiment, the phosphorus - containing acid is the reaction product of one or more of the above polyalkenes and a phosphorus sulfide. Useful phosphorus sulfide sources include phosphorus pentasulfide, phosphorus sesquisulfide, phosphorus heptasulfide and the like. The reaction of the polyalkene and the phosphorus sulfide generally may occur by simply mixing the two at a temperature above 80°C, or from about 100°C to about 300°C. Generally, the products have a phosphorus content from about 0.05% to about 10%, or from about 0.1% to about 5%. The relative proportions of the phosphorizing agent to the olefin polymer is generally from 0.1 part to 50 parts of the phosphorizing agent per 100 parts of the olefin polymer. The phosphorus containing acids are described in U.S. Patent 3,232,883, issued to LeSuer. This reference is herein incorporated by reference for its disclosure to the phosphorus containing acids and methods for preparing the same.

In another embodiment, the acidic organic compound is a phenol. The phenols may be represented by the formula $(R_{28})_a-Ar-(OH)_b$, wherein R_{28} is defined above; Ar is an aromatic group as described above; a and b are independently numbers of at least one, the sum of a and b being in the range of two up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar, which is defined above. In one embodiment, a and b are each independently numbers in the range from one to about four, or from one to about two. In one embodiment, R_{28} and a are such that there is an average of at least about eight aliphatic carbon atoms provided by the R_{28} groups for each phenol compound.

Promoters are often used in preparing the overbased metal salts. The promoters, that is, the materials which facilitate the incorporation of the excess metal into the overbased material, are also quite diverse and well known in the art. A particularly comprehensive discussion of suitable promoters is found in U.S. Patents 2,777,874, 2,695,910, 2,616,904, 3,384,586 and 3,492,231. These patents are incorporated by reference for their disclosure of promoters. In one embodiment, promoters include the alcoholic and phenolic promoters. The alcoholic promoters include the alkanols of one to about 12 carbon atoms, such as methanol, ethanol, amyl alcohol, octanol, isopropanol, and mixtures of these and the like. Phenolic promoters include a variety of hydroxy-substituted benzenes and naphthalenes. A particularly useful class of phenols are the alkylated phenols of the type listed in U.S. Patent 2,777,874, e.g., heptylphenols, octylphenols, and nonylphenols. Mixtures of various promoters are sometimes used.

Acidic materials, which are reacted with the mixture of acidic organic compound, promoter, metal compound and reactive medium, are also disclosed in the above cited patents, for example, U.S. Patent 2,616,904. Those disclosures are incorporated by reference for their disclosure of such acidic materials. Included within the known group of useful acidic materials are liquid acids, such as formic acid, acetic acid, nitric acid, boric acid, sulfuric acid, hydrochloric acid, hydrobromic acid, carbamic acid, substituted carbamic acids, etc. Acetic acid is a very useful

acidic material although inorganic acidic compounds such as HCl, SO₂, SO₃, CO₂, H₂S, N₂O₃, etc., are ordinarily employed as the acidic materials. Particularly useful acidic materials are carbon dioxide and acetic acid.

5 The methods for preparing the overbased materials, as well as overbased materials, are known in the prior art and are disclosed, for example, in the following U.S. Patent Nos.: 2,616,904; 2,616,905; 2,616,906; 3,242,080; 3,250,710; 3,256,186; 3,274,135; 3,492,231; and 4,230,586. These patents disclose processes, materials, which can be overbased, suitable metal bases, promoters, and acidic materials, as well as a variety of specific overbased products useful in
10 producing the overbased systems of this invention and are, accordingly, incorporated herein by reference for these disclosures.

The temperature at which the acidic material is contacted with the remainder of the reaction mass depends to a large measure upon the promoting agent used. With a phenolic promoter, the temperature usually ranges from about 80°C to about
15 300°C, and preferably from about 100°C to about 200°C. When an alcohol or mercaptan is used as the promoting agent, the temperature usually will not exceed the reflux temperature of the reaction mixture and preferably will not exceed about 100°C.

20 In one embodiment, the overbased metal salts are borated overbased metal salts. The borated overbased metals salts are prepared by reacting one or more of the above overbased metals salts with one or more of the above described boron compounds. The borated overbased metal salts generally contains from about 0.1% up to about 15%, or from about 0.5% up to about 10%, or from about 1% up to about 8% by weight of the boron. Borated overbased compositions, lubricating
25 compositions containing the same and methods of preparing borated overbased compositions are found in U.S. Patent 4,744,920, issued to Fischer et al; U.S. Patent 4,792,410 issued to Schwind et al and PCT Publication WO88/03144. The disclosures relating to the above are hereby incorporated by reference.

The following examples relate to borated overbased metal salts and methods of making the same. Unless the context indicates otherwise, here as well as elsewhere in the specification and claims, parts and percentages are by weight, temperature is in degrees Celsius and pressure is atmospheric pressure.

5

Example B-5

(a) A mixture of 853 grams of methyl alcohol, 410 grams of blend oil, 54 grams of sodium hydroxide, and a neutralizing amount of additional sodium hydroxide is prepared. The amount of the latter addition of sodium hydroxide is dependent upon the acid number of the subsequently added sulfonic acid. The temperature of the mixture is adjusted to 49°C. 1070 grams of a mixture of straight chain dialkyl benzene sulfonic acid ($\bar{M}_w=430$) and blend oil (42% by weight active content) are added while maintaining the temperature at 49-57°C. 145 grams of polyisobutenyl (number average $\bar{M}_n=950$)-substituted succinic anhydride are added. 838 grams of sodium hydroxide are added. The temperature is adjusted to 71°C. The reaction mixture is blown with 460 grams of carbon dioxide. The mixture is flash stripped to 149°C, and filtered to clarity to provide the desired product. The product is an overbased sodium sulfonate having a base number (bromophenol blue) of 440, a metal content of 19.45% by weight, a metal ratio of 20, a sulfate ash content of 58% by weight, and a sulfur content of 1.35% by weight.

(b) A mixture of 1000 grams of the product from Example B-5(a) above, 0.13 gram of an antifoaming agent (kerosene solution of Dow Corning 200 Fluid having a viscosity of 1000 cSt at 25°C), and 133 grams of blend oil is heated to 74-79°C with stirring. 486 grams of boric acid are added. The reaction mixture is heated to 121°C to liberate water of reaction and 40-50% by weight of the CO₂ contained in the product from Example 1(a). The reaction mixture is heated to 154-160°C and maintained at that temperature until the free and total water contents are reduced to 0.3% by weight or less and approximately 1-2% by weight, respectively.

The reaction product is cooled to room temperature and filtered. The filtrate has 6.1% boron, 14.4% sodium, and 35% 100 neutral mineral oil.

Example B-6

5 (a) A mixture of 1000 grams of a primarily branched chain monoalkyl benzene sulfonic acid ($\bar{M}_w=500$), 771 grams of o-xylene, and 75.2 grams of polyisobutenyl (number average $\bar{M}_n=950$) succinic anhydride is prepared and the temperature is adjusted to 46°C. 87.3 grams of magnesium oxide are added. 35.8 grams of acetic acid are added. 31.4 grams of methyl alcohol and 59 grams of water are added. The reaction mixture is blown with 77.3 grams of carbon dioxide at a temperature of 49-54°C. 87.3 grams of magnesium oxide, 31.4 grams of methyl alcohol and 59 grams of water are added, and the reaction mixture is blown with 77.3 grams of carbon dioxide at 49-54°C. The foregoing steps of magnesium oxide, methyl alcohol and water addition, followed by carbon dioxide blowing are repeated once. O-xylene, methyl alcohol and water are removed from the reaction mixture using atmospheric and vacuum flash stripping. The reaction mixture is cooled and filtered to clarity. The product is an overbased magnesium sulfonate having a base number (bromophenol blue) of 400, a metal content of 9.3% by weight, a metal ratio 14.7, a sulfate ash content of 46.0%, and a sulfur content of 1.6% by weight.

15 (b) A mixture of 1000 grams of the product from Example B-6(a) and 181 grams of diluent oil is heated to 79°C. Boric acid (300 grams) is added and the reaction mixture is heated to 124°C over a period of 8 hours. The reaction mixture is maintained at 121-127°C for 2-3 hours. A nitrogen sparge is started and the reaction mixture is heated to 149°C to remove water until the water content is 3% by weight or less. The reaction mixture is filtered to provide the desired product. The product contains 7.63% magnesium and 4.35% boron.

Example B-7

(a) A reaction vessel is charged with 281 parts (0.5 equivalent) of a polybutenyl-substituted succinic anhydride derived from a polybutene ($\bar{M}_n=1000$), 281 parts of xylene, 26 parts of tetrapropenyl substituted phenol and 250 parts of 100 neutral mineral oil. The mixture is heated to 80°C and 272 parts (3.4 equivalents) of an aqueous sodium hydroxide solution are added to the reaction mixture. The mixture is blown with nitrogen at 1 scfh (standard cu. ft/hr) and the reaction temperature is increased to 148°C. The reaction mixture is then blown with carbon dioxide at 1 scfh for one hour and 25 minutes while 150 parts of water is collected. The reaction mixture is cooled to 80°C where 272 parts (3.4 equivalents) of the above sodium hydroxide solution is added to the reaction mixture and the mixture is blown with nitrogen at 1 scfh. The reaction temperature is increased to 140°C where the reaction mixture is blown with carbon dioxide at 1 scfh for 1 hour and 25 minutes while 150 parts of water is collected. The reaction temperature is decreased to 100°C and 272 parts (3.4 equivalents) of the above sodium hydroxide solution is added while blowing the mixture with nitrogen at 1 scfh. The reaction temperature is increased to 148°C and the reaction mixture is blown with carbon dioxide at 1 scfh for 1 hour and 40 minutes while 160 parts of water is collected. The reaction mixture is cooled to 90°C and where 250 parts of 100 neutral mineral oil are added to the reaction mixture. The reaction mixture is vacuum stripped at 70°C and the residue is filtered through diatomaceous earth. The filtrate contains 50.0% sodium sulfate ash (theoretical 53.8%) by ASTM D-874, total base number of 408, a specific gravity of 1.18 and 37.1% oil.

(b) A reaction vessel is charged with 700 parts of the product of Example B-7(a). The reaction mixture is heated to 75°C where 340 parts (5.5 equivalents) of boric acid is added over 30 minutes. The reaction mixture is heated to 110°C over 45 minutes and the reaction temperature is maintained for 2 hours. A 100 neutral mineral oil (80 parts) is added to the reaction mixture. The reaction mixture is blown with nitrogen at 1 scfh at 160°C for 30 minutes while 95 parts of water is

collected. Xylene (200 parts) is added to the reaction mixture and the reaction temperature is maintained at 130-140°C for 3 hours. The reaction mixture is vacuum stripped at 150°C and 20 millimeters of mercury. The residue is filtered through diatomaceous earth. The filtrate contains 5.84% boron (theoretical 6.43) and 33.1% oil. The residue has a total base number of 309.

In another embodiment, the boron compound is a borated epoxide. The borated fatty epoxides are generally the reaction product of one or more of the above boron compounds with at least one epoxide. The epoxide is generally an aliphatic epoxide having from 8 to about 30, or from about 10 to about 24, from about 12 to about 20 carbon atoms. Examples of useful aliphatic epoxides include heptyl epoxide, octyl epoxide, oleyl epoxide and the like. Mixtures of epoxides may also be used, for instance commercial mixtures of epoxides having from about 14 to about 16 carbon atoms and from about 14 to about 18 carbon atoms. The borated fatty epoxides are generally known and are disclosed in U.S. Patent 4,584,115. This patent is incorporated by reference for its disclosure of borated fatty epoxides and methods for preparing the same.

In one embodiment, the boron compound is a borate ester. The borate esters may be prepared by reacting of one or more of the above boron compounds with one or more of the above alcohols. Typically, the alcohols contain from about 6 to about 30, or from about 8 to about 24 carbon atoms. The methods of making such borate esters are known to those in the art.

In another embodiment, borate ester is a borated phospholipid. The borated phospholipids are prepared by reacting a combination of a phospholipid and a boron compound. Optionally, the combination may include one or more of the above amines, acylated nitrogen compounds, carboxylic esters, Mannich reaction products, neutral or basic metal salts of an organic acid compounds, or mixtures of two or more thereof. These additional components are described above. Phospholipids, sometimes referred to as phosphatides and phospholipins, may be natural or synthetic. Naturally derived phospholipids include those derived from

fish, fish oil, shellfish, bovine brain, chicken egg, sunflowers, soybean, corn, and cottonseeds. Phospholipids may be derived from microorganisms, including blue-green algae, green algae, and bacteria.

The reaction of the phospholipid and the boron compound usually occurs at a temperature from about 60°C to about 200°C, or from about 90°C to about 150°C. The boron compound and phospholipid are reacted at an equivalent ratio of boron to phosphorus of about 1-6:1 or about 2-4:1, or about 3:1. When the combination includes additional components (e.g. amines, acylated amines, neutral or basic meal salts, etc.), the boron compound is reacted with the mixture of the phospholipid and one or more optional ingredients in an amount of one equivalent of boron to an equivalent of the mixture of a phospholipid and an optional ingredient in a ratio from about one, or about two to about six, to about four to one. The equivalents of the mixture are based on the combined equivalents of phospholipid based on phosphorus and equivalents of the optional ingredients.

Antioxidants (D)

In another embodiment, the lubricating compositions and the concentrates may contain (D) one or more antioxidant. In one embodiment, the antioxidant is present in an amount from about 0.001% to about 5%, or from about 0.01% to about 2%, or from about 0.05% to about 1% by weight of the lubricating composition. The antioxidants may be present in a total amount generally from about 1.5% up to about 10%, or about 1.8% up to about 8%, or from about 1.9% up to about 6% by weight. In another embodiment, the lubricating composition contains at least about 1% by weight of an amine antioxidant, a dithiocarbamate antioxidant, or mixture thereof. In this embodiment, the lubricating compositions have at least about 1%, or from about 1.5%, or from about 1.7% by weight of an amine antioxidant, a dithiocarbamate antioxidant, or mixture thereof, preferably an amine antioxidant. In another embodiment, the antioxidant is present in an amount to deliver at least about 0.04%, or at least about 0.05%, or at least about 0.07% by

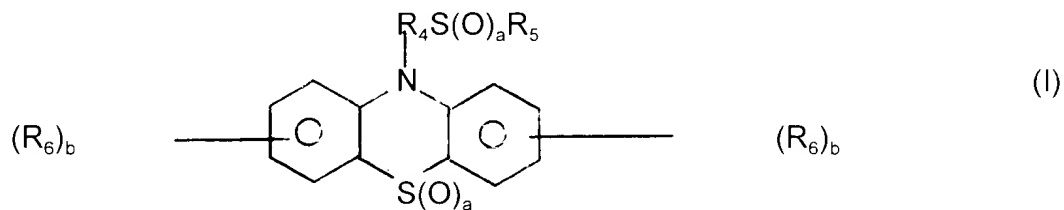
weight nitrogen to the fully formulated lubricant. In another embodiment, the antioxidant include amine antioxidants, dithiophosphoric acid esters, phenol antioxidants, dithiocarbamates, phosphite antioxidants, sulfurized Diels-Alder adducts, and mixtures thereof. In one embodiment, the antioxidant is an amine antioxidant, or a dithiocarbamate antioxidant. In one embodiment, the antioxidants are ashless, i.e., free of metal. In another embodiment the antioxidant is other than a polyphenol.

Amine antioxidants include alkylated aromatic amines and heterocyclic amines. The alkylated aromatic amines include compounds represented by the formula $Ar^1-NR_1-Ar^2$, wherein Ar^1 and Ar^2 are independently mononuclear or polynuclear, substituted or unsubstituted aromatic groups; and R_1 is hydrogen, halogen, OH, NH_2 , SH, NO_2 or a hydrocarbyl group having from 1 to about 50 carbon atoms. The aromatic group as represented by "Ar", as well as elsewhere in other formulae in this specification and in the appended claims, may be mononuclear or polynuclear. Examples of mononuclear Ar moieties include benzene moieties, such as 1,2,4-benzenetriyl; 1,2,3-benzenetriyl; 3-methyl-1,2,4-benzenetriyl; 2-methyl-5-ethyl-1,3,4-benzenetriyl; 3-propoxy-1,2,4,5-benzenetetrail; 3-chloro-1,2,4-benzenetriyl; 1,2,3,5-benzenetetrail; 3-cyclohexyl-1,2,4-benzenetriyl; and 3-azocyclopentyl-1,2,5-benzenetriyl, and pyridine moieties, such as 3,4,5-azabenzene; and 6-methyl-3,4,5-azabenzene. The polynuclear groups may be those where an aromatic nucleus is fused at two points to another aromatic nucleus, such as naphthyl and anthracenyl groups. Specific examples of fused ring aromatic moieties Ar include: 1,4,8-naphthylene; 1,5,8-naphthylene; 3,6-dimethyl-4,5,8(1-azonaphthalene); 7-methyl-9-methoxy-1,2,5, 9-anthracenetetrail; 3,10-phenathrylene; and 9-methoxy-benz(a)phenanthrene-5,6,8,12-yl. The polynuclear group may be those where at least two nuclei (either mononuclear or polynuclear) are linked through bridging linkages. These bridging linkages may be chosen from the group consisting of alkylene linkages, ether linkages, keto linkages, sulfide linkages, and polysulfide linkages of 2 to about 6 sulfur atoms. Specific examples

of Ar when it is linked polynuclear aromatic moiety include: 3,3',4,4',5-bibenzenetetrayl; di(3,4-phenylene)ether; 2,3-phenylene-2,6-naphthylenemethane; and 3-methyl,9H-fluorene-1,2,4,5,8-yl; 2,2-di(3,4-phenylene)propane; sulfur-coupled 3-methyl-1,2,4-benzatriyl (having 1 to about 10 thiomethylphenylene groups); and amino-coupled 3-methyl-1,2,4-benzatriyl (having 1 to about 10 aminomethylphenylene groups). Typically Ar is a benzene nucleus, lower alkylene bridged benzene nucleus, or a naphthalene nucleus.

In another embodiment, the alkylated aromatic amine is represented by the formula $R_2\text{-Ar-NH-Ar-R}_3$, wherein R_2 and R_3 are independently hydrogen or hydrocarbonyl groups having from 1 to about 50, or from about 4 to about 20 carbon atoms. Examples of aromatic amines include p,p'-dioctyldiphenylamine; octylphenyl-beta-naphthylamine; octylphenyl- α -naphthylamine, phenyl- α -naphthylamine; phenyl-beta-naphthylamine; p-octylphenyl- α -naphthylamine and 4-octylphenyl-1-octyl-beta-naphthylamine and di(nonylphenyl)amine, with di(nonylphenyl)amine preferred. U.S. Patents 2,558,285; 3,601,632; 3,368,975; and 3,505,225 disclose diarylamines useful as antioxidant (D). These patents are incorporated herein by reference.

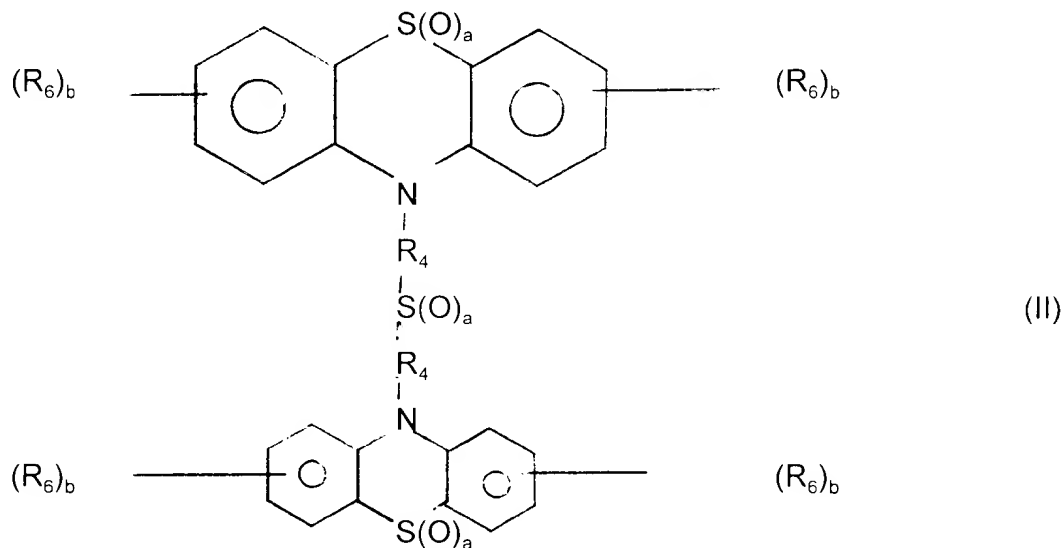
In another embodiment, the antioxidant (D) may be a phenothiazine. Phenothiazines include phenothiazine, substituted phenothiazine, or derivatives, such as those represented by the formula



wherein R_4 is an alkylene, alkenylene or an aralkylene group, or mixtures thereof, R_5 is selected from the group consisting of higher alkyl groups, or an alkenyl, aryl,

alkaryl or aralkyl group and mixtures thereof; each R_6 is independently alkyl, alkenyl, aryl, alkaryl, arylalkyl, halogen, hydroxyl, alkoxy, alkylthio, arylthio, or fused aromatic rings, or mixtures thereof; a and b are each independently 0 or greater. In one embodiment, R_4 contains from about 2 to about 8, or two or three carbon atoms. R_5 typically contains from about 3 to about 30, or from about 4 to about 15 carbon atoms. R_6 contains from 1 to about 50, or from about 4 to about 30, or from 6 to about 20 carbon atoms.

In another embodiment, the phenothiazine derivatives may be represented by the formula



wherein R_4 , R_6 , a and b are as defined with respect to Formula I.

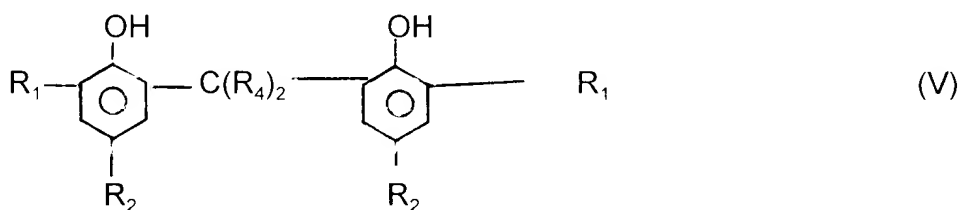
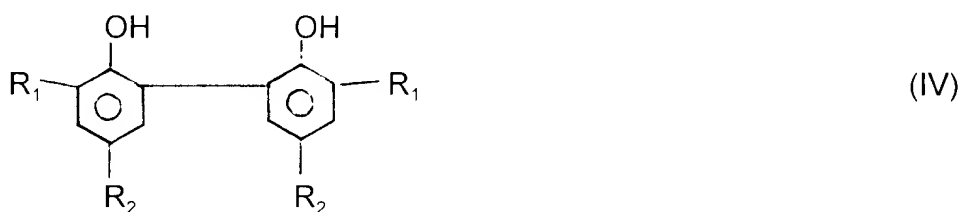
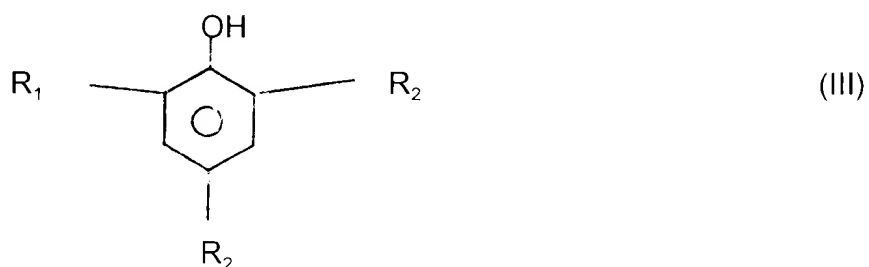
The above-described phenothiazine derivatives, and methods for their preparation are described in U.S. Patent 4,785,095, and the disclosure of this patent is hereby incorporated by reference for its teachings of such methods and compounds. In one embodiment, a dialkyldiphenylamine is treated with sulfur at an elevated temperature such as in the range of 145°C to 205°C for a sufficient time to complete the reaction. A catalyst such as iodine may be utilized to establish the sulfur bridge.

Phenothiazine and its various derivatives may be converted to the above compounds by contacting the phenothiazine compound containing the free NH group with a thioalcohol of the formula R_5SR_4OH where R_4 and R_5 are defined with respect to Formula I. The thioalcohol may be obtained by the reaction of a mercaptan (e.g. a C_{4-30} mercaptan), such as hexanethiol, octanethiol and dodecanethiol, with an alkylene oxide, such as ethylene or propylene oxide under basic conditions. Alternatively, the thioalcohol may be obtained by reacting a terminal olefin, such as those described herein, with mercaptoethanol under free radical conditions. When it is desired to prepare compounds of the type represented by Formulae I and II wherein a is 1 or 2, i.e., sulfones or sulfoxides, the derivatives prepared by the reaction with the thioalcohols described above are oxidized with an oxidizing agent, such as hydrogen peroxide, in a solvent such as glacial acetic acid or ethanol under an inert gas blanket. The partial oxidation takes place conveniently at from about $20^{\circ}C$ to about $150^{\circ}C$.

In one embodiment, the antioxidant may be one or more of the above phosphorus esters which are reaction products of one or more of the above phosphorus reagents and one or more of the above unsaturated compounds. The thiophosphorus acid esters may be mono- or dithiophosphorus acid esters. Thiophosphorus acid esters are also referred to generally as dithiophosphates.

The reaction products of phosphoric acids and an unsaturated amide are referred to as phosphorus containing amides. An example of such reaction product is the reaction of methylamyl dithiophosphoric acid or isooctyl, isopropyl dithiophosphoric acid and acrylamide. The phosphorus containing amides are known in the art and are disclosed in U.S. Patents 4,670,169, 4,770,807, and 4,876,374 which are incorporated by reference for their disclosures of phosphorus amides and their preparation. Examples of reaction products of a phosphoric acid and an unsaturated ester are the reaction product of isobutyl, amyl dithiophosphoric acid and methyl acrylate and di(amyl)dithiophosphoric acid and butyl methacrylate.

In another embodiment, the antioxidant (A) is at least one phenol antioxidant. The phenol antioxidants include metal and metal free hindered phenols. Alkylene coupled derivatives of hindered phenols and phenol sulfides or sulfur coupled phenols may also be used. Hindered phenols are defined as those containing a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds wherein the hydroxyl groups are in the o- or p-position to each other. The metal-free hindered phenols may be represented by the following formulae:



25

wherein each R_1 is independently a hydrocarbyl group containing from 3 to about 9 carbon atoms, each R_2 is hydrogen or a hydrocarbyl group, R_3 is hydrogen or a hydrocarbyl group containing from 1 to about 9 carbon atoms, and each R_4 is independently hydrogen or a methyl group. In one embodiment, R_2 is an alkyl

group containing from about 3 to about 50, or from about 6 to about 20, or from about 6 to about 12 carbon atoms. In one embodiment alkyl groups are derived from one or more of the above polyalkenes. The alkyl groups may be derived from polymers of ethylene, propylene, 1-butene and isobutene, preferably propylene tetramer or trimer. Examples of R_2 groups include hexyl, heptyl, octyl, decyl, dodecyl, tripropenyl, tetrapropenyl, etc. Examples of R_1 , R_2 and R_3 groups include propyl, isopropyl, butyl, sec-butyl, tert-butyl, heptyl, octyl, and nonyl. In another embodiment, each R_1 and R_3 are tertiary groups, such as tert-butyl or tert-amyl groups. The phenolic compounds may be prepared by various techniques, and in one embodiment, such phenols are prepared in stepwise manner by first preparing the para-substituted alkylphenol, and thereafter alkylating the para-substituted phenol in the 2- and/or 6-position as desired. When it is desired to prepare coupled phenols of the type represented by Formulae IV and V, the second step alkylation is conducted under conditions which result in the alkylation of only one of the positions ortho to the hydroxyl group. Examples of useful phenolic materials include: 2-t-butyl-4-heptylphenol; 2-t-butyl-4-octylphenol; 2-t-butyl-4-dodecylphenol; 2,6-di-t-butyl-4-butylphenol; 2,6-di-t-butyl-4-heptylphenol; 2,6-di-t-butyl-4-dodecylphenol; 2,6-di-t-butyl-tetrapropenylphenol; 2-methyl-6-di-t-butyl-4-heptylphenol; 2,6-di-t-butyl-tripropenylphenol; 2,4-dimethyl-6-t-butylphenol; 2,6-t-butyl-4-ethylphenol; 4-t-butyl catechol; 2,4-di-t-butyl-p-cresol; 2,6-di-t-butyl-4-methylphenol; and 2-methyl-6-di-t-butyl-4-dodecylphenol. Examples of the ortho coupled phenols include: 2,2'-bis(6-t-butyl-4-heptylphenol); 2,2'-bis(6-t-butyl-4-octylphenol); 2,6-bis-(1'-methylcyclohexyl)-4-methylphenol; and 2,2'-bis(6-t-butyl-4-dodecylphenol).

Alkylenecoupled phenolic compounds may be prepared from the phenols by reaction of the phenolic compound with an aldehyde, typically those containing from one to about eight carbon atoms, such as formaldehyde or acetaldehyde, aldehyde precursors, such as paraformaldehyde or trioxane, or a ketone, such as acetone. The alkylenecoupled phenols may be obtained by reacting from 0.3 to about 2

moles a phenol with 1 equivalent of an aldehyde or ketone. Procedures for coupling of phenolic compounds with aldehydes and ketones are known to those in the art. Examples of phenolic compounds include 2,2'-methylenebis(6-t-butyl-4-heptylphenol); 2,2'-methylenebis(6-t-butyl-4-octylphenol); 2,2'-methylenebis(4-dodecyl-6-t-butylphenol); 2,2'-methylenebis(4-octyl-6-t-butylphenol); 2,2'-methylenebis(4-octylphenol); 2,2'-methylenebis(4-dodecylphenol); 2,2'-methylenebis(4-heptylphenol); 2,2'-methylenebis(6-t-butyl-4-dodecylphenol); 2,2'-methylenebis(6-t-butyl-4-tetrapropenylphenol); and 2,2'-methylenebis(6-t-butyl-4-butyl phenol).

In another embodiment, the antioxidant (D) is a metal-free (or ashless) alkylphenol sulfide or sulfur coupled phenols. The alkylphenols from which the sulfides are prepared also may comprise phenols of the type discussed above and represented by Formula III wherein R_3 is hydrogen. For example, the alkylphenols which can be converted to alkylphenol sulfides include: 2-t-butyl-4-heptylphenol; 2-t-butyl-4-octylphenol; and 2-t-butyl-4-dodecylphenol; 2-t-butyl-4-tetrapropenylphenol. The term "alkylphenol sulfides" is meant to include di-(alkylphenol) monosulfides, disulfides, and polysulfides, as well as other products obtained by the reaction of the alkylphenol with sulfur monochloride, sulfur dichloride or elemental sulfur. One mole of phenol typically is reacted with about 0.5-1.5 moles, or higher, of sulfur compound. For example, the alkylphenol sulfides are readily obtained by mixing, one mole of an alkylphenol and 0.5-2.0 moles of sulfur dichloride. The reaction mixture is usually maintained at about 100°C for about 2-5 hours, after which time the resulting sulfide is dried and filtered. When elemental sulfur is used, temperatures from about 150-250°C or higher are typically used. It is also desirable that the drying operation be conducted under nitrogen or a similar inert gas. A particularly useful alkylphenol sulfide is thio-bis(tetrapropenylphenate).

Suitable basic alkylphenol sulfides are disclosed, for example, in U.S. Patents 3,372,116; 3,410,798; and 4,021,419, which are hereby incorporated by reference.

These sulfur-containing phenolic compositions described in U.S. Patent 4,021,419 are obtained by sulfurizing a substituted phenol with sulfur or a sulfur halide and thereafter reacting the sulfurized phenol with formaldehyde or an aldehyde precursor, e.g., paraformaldehyde or trioxane. Alternatively the substituted phenol may be first reacted with formaldehyde or paraformaldehyde and thereafter reacted with sulfur or a sulfur halide to produce the desired alkylphenol sulfide.

In another embodiment, the antioxidant (D) is a dithiocarbamate antioxidant. The dithiocarbamate antioxidants include reaction products of a dithiocarbamic acid or salt and one or more of the above described unsaturated compounds, such as unsaturated amides, carboxylic acids, anhydrides, or esters, or ethers; alkylene-coupled dithiocarbamates; and bis(S-alkyldithiocarbamoyl) disulfides. In one embodiment, the dithiocarbamate compounds are ashless, i.e. metal free. The dithiocarbamates are described above.

In another embodiment, antioxidant is a sulfurized Diels-Alder adduct. The Sulfurized Diels-Alder adduct and its preparation are described above.

Other Additives

The invention also contemplates the use of other additives, such as, for example, detergents and dispersants, corrosion- and oxidation-inhibiting agents, pour point depressing agents, extreme pressure agents, auxiliary antiwear agents, color stabilizers and anti-foam agents. The dispersant includes carboxylic dispersants (e.g. acylated amines and carboxylic esters), amine dispersants, Mannich dispersants, post treated dispersants and polymer dispersants. The carboxylic, amine and Mannich dispersants are discussed above.

Post-treated dispersants are obtained by reacting at carboxylic, amine or Mannich dispersants with reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in the following U.S. Patents:

3,200,107, 3,282,955, 3,367,943, 3,513,093, 3,639,242, 3,649,659, 3,442,808, 3,455,832, 3,579,450, 3,600,372, 3,702,757, and 3,708,422, the disclosures of which is hereby incorporated by reference.

5 Polymeric dispersants are interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. Examples of polymer dispersants thereof are disclosed in the following U.S. Patents: 3,329,658, 3,449,250, 3,519,6-
10 56, 3,666,730, 3,687,849, and 3,702,300, the disclosures of which is hereby incorporated by reference.

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15 thereof are disclosed in the following U.S. Patents: 3,329,658, 3,449,250, 3,519,6-56, 3,666,730, 3,687,849, and 3,702,300, the disclosures of which is hereby incorporated by reference.

In one embodiment, the lubricants may include an overbased metal salt of an acidic organic compounds. These materials are described above, the disclosure of
20 which is incorporated here by reference. These overbased salts do not contain boron.

In one embodiment, the lubricating compositions and functional fluids contain one or more auxiliary extreme pressure and/or antiwear agents, corrosion inhibitors and/or oxidation inhibitors. Many of the above-mentioned extreme pressure agents
25 and corrosion-oxidation inhibitors also serve as antiwear agents. In one embodiment, the lubricants are free of metal dithiophosphates, such as zinc dithiophosphates and/or chlorinated hydrocarbons, such as chlorinated wax.

The lubricating compositions and functional fluids may contain one or more pour point depressants, color stabilizers, metal deactivators and/or anti-foam

agents. Pour point depressants are a particularly useful type of additive often included in the lubricating oils described herein. The use of such pour point depressants in oil-based compositions to improve low temperature properties of oil-based compositions is well known in the art. See, for example, page 8 of "Lubricant Additives" by C.V. Smalheer and R. Kennedy Smith (Lezius-Hiles Co. publishers, Cleveland, Ohio, 1967). Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 which are herein incorporated by reference for their relevant disclosures.

In one embodiment, the pour point depressant is represented by the general structural formula: $\text{Ar(R)}-(\text{Ar}'(\text{R}'))-\text{Ar}''$, wherein the Ar, Ar' and Ar'' are the same as "Ar" discussed above, (R) and (R') are independently an alkylene group containing 1 to 100 carbon atoms with the proviso that at least one of (R) or (R') is CH_2 , and n is 0 to about 1000 with the proviso that if 'n is 0, then (R) is CH_2 and at least one aromatic moiety has at least one substituent, the substituents being selected from the group consisting of a substituent derived from an olefin (preferably an olefin containing about 8 to about 30 carbon atoms, more preferably about 16-18 carbon atoms) and a substituent derived from a chlorinated hydrocarbon preferably containing about 8 to about 50 carbon atoms more preferably containing about 24 carbon atoms and about 2.5 chlorine atoms for each 24 carbon atoms.

Anti-foam agents are used to reduce or prevent the formation of stable foam. Typical anti-foam agents include silicones or organic polymers. Additional anti-foam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

These additional additives, when used, are present in the inventive lubricating and functional fluid compositions at sufficient concentrations to provide the compositions with enhanced properties depending upon their intended use. Generally, each of these additional additives are present in the lubricants and functional fluids at concentrations from about 0.01%, or from about 0.05%, or from about 0.5%. These additional additives are generally present in an amount up to about 20% by weight, or up to about 10% by weight, and or up to about 3% by weight.

The substituents for the aromatic moieties are obtained from olefins and/or chlorinated hydrocarbons, e.g., chlorinated wax. The olefins are described above. A particularly preferred chlorinated hydrocarbon, being one of about 24 carbons containing about 2.5 chlorines per 24 carbon atoms.

The desired material is a mixture of products which include alkylated naphthalenes, coupled and bridged naphthalenes, oligomers and dehydrohalogenated waxes. The molecular weight distribution of the final product is a more useful characterization of the final product. A useful molecular weight range is from about 300-2000. A more useful molecular weight range is from 500 to 10,000. A preferred distribution is from 400 to 112,000. The most useful distribution is from about 271 to about 300,000. U. S. Patents 1,667,214, issued to Michel; 1,815,022, issued to Davis, and 4,753,745, issued to Kostusyk et al teach such alkylated aromatic compounds useful as pour point depressants. These patents are incorporated by reference.

In another embodiment, the pour point depressant is a ester of a carboxy containing interpolymers of an vinyl aromatic compound, (discussed above), e.g., styrene and an unsaturated carboxylic reagents (discussed above), e.g, maleic anhydride. The pour point depressant are generally referred to a maleic anhydride-styrene copolymer pour point depressants. These polymers are described in U.S. Patents 4,284,414, 4,604,221 and 5,338,471, whose disclosure are hereby incorporated by reference.

In one embodiment, the oil of lubricating viscosity are selected to provide lubricating compositions with a kinematic viscosity of at least about 3.5 cSt, or at least about 4.0 cSt at 100°C. In one embodiment, the lubricating compositions have an SAE gear viscosity number of at least about SAE 70W, or at least about SAE 75W. The lubricating composition may also have a so-called multigrade rating such as SAE 75W-80, 75W-90, 75W-90, 75W-140, 80W-90, or 80W-140. Multigrade lubricants may include a viscosity improver which is formulated with the oil of lubricating viscosity to provide the above lubricant grades.

The above-described mineral oil may be used with commercially available gear and transmission concentrates such as those sold by Exxon, Lubrizol, Ethyl and Mobil corporations. In this embodiment, those commercial concentrates are diluted with the basestocks to form the transmission and gear formulations.

In one embodiment, the lubricating compositions contain less than 2%, or less than 1.5%, or less than 1% by weight of a dispersant. In another embodiment, the lubricating compositions are free of lead based additives, metal (zinc) dithiophosphates, and alkali or alkaline earth metal borates.

In one embodiment, the lubricating compositions of the present invention are free to Group II basestocks. In another embodiment, the lubricating compositions are free of polyalphaolefin basestocks. In another embodiment, the lubricating compositions include a Group III brightstock. In yet another embodiment, the basestock is comprised of greater than 80%, or greater than 90% by weight of a Group III basestock.

The following examples relate to lubricating compositions which are gear oils and transmission fluids. Here, as well as elsewhere in the specification and claims, unless otherwise indicated, the amounts and percentages are by weight, the temperature is degrees celcius, and the pressure is atmospheric pressure.

Example 1

A lubricant is prepared by incorporating 3.5% by weight of the product of Example S-1 and 23.6% of polyisobutene ($\bar{M}_w = 6700$) into TEXHVI-100 neutral oil.

5

Example 2

A lubricant is prepared as described in Example 1 except 1.2% of the product of Example P-3 is used in place of the product of Example S-1.

Example 3

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A lubricant is prepared as described in Example 1 except that 1.2% of a borated overbased synthetic alkyl benzene sulfonate (6.9% magnesium, metal ratio of 14.7, and a total base number (bromophenyl blue) of 295) is used in place of the product of Example S-1.

15

Example 4

The lubricant is prepared by incorporating the product of Example S-1 (3.2%) the product of Example P-3 (1.2%) 23.6% polyisobutylene, and 8% Alkylate A-230 into a Chevron UCBO 4 cSt.

20

Examples 5

The lubricant is prepared as described in Example 2 except that the borated overbased product (1.2%) is added to the lubricant of Example 2.

Examples 6-10

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Examples 6-10 are further examples of lubricating compositions which are blended with Chevron UCBO 4 centistoke Group III basestock.

	6	7	8	9	10
Dinonyldiphenylamine		--	--	3.5	3.5
Borated overbased product of Example 3	1.2	--	--	1.2	--
Oleylamide	—	0.1	0.09	—	0.1
Product of Ex S-1	3.5	3.75	3.2	3.5	3.5
Product of Ex P-3	1.3	1.3	1.2	1.3	1.3
Reaction product of polybutenyl ($\bar{M}_n=850$) succinic anhydride and tetraethylene pentamine	1.0	—	—	1	--
Silicon antifoam	0.002	—		0.02	--
Borated dispersant		—	1.1	—	1.1
Triphenyl phosphite	0.27	—		0.27	--
Glycerol monooleate	0.25	—		0.25	--
DMTD product	0.86 ¹	0.15 ²	0.1 ²	0.80 ¹	0.1 ²
0942.8	—	—	0.005	—	0.005

- 1) Blend of dimercaptiothiadiazole and a reaction product of polyisobutenyl succinic anhydride esterified with pentaerythritol, and then polyamines.
- 2) Reaction product of dimercaptiothiadiazole, formaldehyde and heptylphenol.

Example 11

A lubricant is prepared by blending 0.33 parts of overbased calcium alkyl benzene sulfonate (28% diluent, 12% calcium, metal ratio of 11 and a TBN of 300), 0.92 parts of neutral calcium alkyl benzene sulfonate (50% diluent oil, 2.5% calcium

and a TBN of 13), 2.73 parts of the reaction product of polyisobutenyl (\bar{M}_n 950) succinic anhydride and condensed polyamine (40% diluent oil, 1.6% nitrogen, and TBN 35), 0.55 parts of borated dispersant prepared by reacting boric acid with a reaction product of a polyisobutyl (\bar{M}_n 950) succinic anhydride and a condensed polyamine (33% diluent oil, 2.3% nitrogen, 1.9% boron), 0.09 parts of dioleylphosphite, 0.05 parts of silicone antifoam agent, 0.55 parts of a carbon disulfide reaction product of a dispersant prepared from polyisobutyl (\bar{M}_n 950) and a condensed polyamine (42% diluent, 1.5% nitrogen, 1.0% sulfur and a TBN of 14), 0.03 parts of a reaction product of dimercaptiothiadiazole, formaldehyde and heptylphenol, 0.43 parts of an alkylated reaction product of nonenes and diphenylamine (3.9% N), 0.55 parts of the reaction product of propylene oxide and t-dodecyl mercaptan and 12.6 parts of by weight of LZ 7720C and 0.2 parts of Garbacryl 6335 are added to a mixture of 80% by weight MOTIVA TEX HVI 3 cSt and 20% by weight MOTIVA TEX HVI 4 cSt.

Example 10

A lubricant is prepared as described in Example 9 except no Garbacryl 6335 is present and the additives are blended into a mixture of 65% by weight Petro Canada VHVI 4 cSt and 35% by weight Petro Canada VHVI 2 cSt.

Example 11

A lubricant is prepared by blending 0.11 parts of dibutyl hydrogen phosphite, 0.1 parts of phosphoric acid (15% H_2O), 1 parts of the reaction product of dimercaptiothiadiazole with an ester dispersant as described in Example 4, 0.6 parts of an alkylated reaction product of nonenes and diphenylamine (3.9% N), 0.5 parts of the reaction product of propylene oxide and t-dodecyl mercaptan, 0.03 parts of an oxidatively coupled dimercaptiothiadiazole and nonyl mercaptan, 0.2 parts of the reaction product of C_{16} alpha epoxide with boric acid, 0.7 parts of 100 neutral diluent oil, 0.4 parts of 3-decloxysulfolane, 0.1 parts of Ethomeen T-12, 0.23 parts of an

overbased calcium alkyl benzene sulfonate (42% diluent, 12% Ca, metal ratio 11, and 300 TBN), 4 parts of the reaction product of polyisobutenyl (\bar{M}_n 950) succinic anhydride and condensed polyamines (40% diluent, 2.2% nitrogen and TBN of 48), 300 ppm of a silicone antifoam agent, 10.5 parts of LZ 7720C, 0.1 parts Viscoplex 1-3006 into Chevron UCBO 4 cSt.

Example 12

A lubricant is prepared as described in Example 8 except 10.5 parts of LZ 7720C is used, 0.1 parts of Acryloid 3008, available from Rohm and Haas, is used in place of Viscoplex 6335 and the Chevron UCBO is replaced by a mixture of 50% by weight Yubase 4 cSt and 50% by weight is Yubase 3 cSt.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.